ADSORPTION OF UREA BY SOILS, CLAY MINERALS AND OXIDES OF IRON AND ALUMINIUM

By

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ABSTRACT

Soils, the clary minerals bentonite, kaolinite and also oxides of iron and aluminium have been found to possess adsorptive capacities for urea from solutions. The percentage of urea adsorbed from the added amount is considerable at low concentration, when added to the above materials. No increase in the adsorption of urea or the liberation of calcium is observed as a result of application of excess of urea.

Urea as a fertilizer is getting more and more attention these days. The high nitrogen content together with the facility with which this fertilizer is manufactured lend it a great support to be used as a nitrogeneous fertilizer. Though great losses from urine, when added to the compost heaps or to the soils, have been observed by various workers, little work seems to have been done to find out the adsorption and retention of urea by the soils or clay minerals. However, Cheldelin and Williams[1] have reported the adsorption of urea by activated charcoal and have found that the Freundlich's equation is applicable.

The present studies were carried out with a view to find out the amount of urea adsorbed by soils, clay minerals and oxides of iron and aluminium under laboratory conditions.

The materials used for adsorption experiments were, two samples of soils, (S₁, S₂), one of bentonite (Kashmir) and one of kaolin (E. Merck.) and also iron oxide and aluminium oxide. They were finely powdered and then passed through a 100 mesh seive. After oven-drying, they were stored in corked bottles and used for the adsorption experiments. 5 gms. of each material were taken and 100 ml. of different concentrations of urea solution varying from 0·1M to 0·01M were added. The contents were shaken in corked conical flasks for one hour and allowed to stand for 24 hours. The supernatant liquid was separated by filtering it through Buchner funnel using suction. First few ml. of the filtrates were rejected and then the filtrates were analysed for the urea contents. The original solutions were also analysed for their urea contents using the sodium hypobromite method.[2] The amount of N_2 evolved was measured and from it the amounts of urea were calculated. The differences in the concentrations of original and the equilibrium solutions were taken as the quantities of urea adsorbed. The adsorption was calculated per 100 gms. of the respective adsorbents.

Calcium derivatives of soil, bentonite, and kaolinite were then prepared by treating the materials with $N.CaCl_2$ and then freeing the excess calcium chloride with distilled water. Then these materials were air-dried, powered, oven-dried and then finally used for adsorption studies as before.

The amount of calcium given out with different concentrations of urea have been estimated in the filtrates and reported. The amounts of calcium given out by the materials by using distilled water alone have also been given.

The soils were collected from Allahabad University grounds and analysed for their total carbon and calcium contents. They contained carbon and calcium as follows :

	Carbon	Calcium
Sample (S₁)	0·4%	1·0%
Sample (S₂)	1·4%	4·0%

TABLE 1 (a)

Adsorption of Urea by Bentonite and Soil (S₁)

	Original Conc. of Urea (M)	Equilibrium concentration of Urea (M)		Urea adsorbed per 100 gms. of the materials. (gms.)	
		Bentonite	Soil S₁	Bentonite	Soil (S₁)
1.	0·1162	0·1113	0·1162	0·0586	nil
2.	0·0600	0·04149	0·0600	0·0222	nil
3.	0·045887	0·04003	0·045887	0·0702	nil
4.	0·02392	0·01952	0·023432	0·0527	0·0058
5.	0·01611	0·011716	0·015133	0·0527	0·0117
6.	0·011228	0·008784	0·009275	0·0293	0·0234

TABLE 1 (b)

Adsorption of Urea by Al_2O_3

	Original Conc. of Urea (M)	Equilibrium conc. of Urea (M)	Urea adsorbed per 100 gms. of the material (gm.)
1.	0·1188	0·11667	0·0254
2.	0·06004	0·057604	0·0293
3.	0·045887	0·044435	0·0351
4.	0·023432	0·021967	0·0176
5.	0·01611	0·012692	0·0410
6.	0·011228	0·009275	0·0234

TABLE 1 (c)

Adsorption of Urea by Fe_2O_3.

	Original conc. of Urea (M)	Equilibrium conc. of Urea (M)	Urea adsorbed per 100 gms. of the material. (gms.)
1.	0·1188	0·11716	0·0216
2.	0·05614	0·05467	0·0176
3.	0·045887	0·045399	0·0058
4.	0·023920	0·020508	0·0410
5.	0·01611	0·014157	0·0234
6.	0·014645	0·011228	0·0176

TABLE 1 (d)

Adsorption of Urea by Soil (S_2)

	Original Conc. of Urea (M)	Equilibrium conc. of Urea (M)	Urea adsorbed per 100 gms. of the material. (gms.)
1.	0·108861	0·105932	0·0351
2.	0·056140	0·055163	0·0117
3.	0·04833	0·04393	0·0527
4.	0·023432	0·022944	0·0058
5.	0·014322	0·012205	0·0234
6.	0·010739	0·00976	0·0117

TABLE 1 (e)

Adsorption of Urea by Kaolinite

	Original conc. of Urea (M)	Equilibrium conc. of Urea (M)	Urea adsorbed per 100 gms. of the material. (gms.)
1.	0·104956	0·104956	nil
2.	0·059723	0·046342	0·1585
3.	0·045887	0·043930	0·0234
4.	0·025384	0·022944	0·0293
5.	0·015133	0·011716	0·0410
6.	0·010739	0·008299	0·0293

TABLE 2

Adsorption of Urea by Ca-Bentonite, Ca-Kalinite and Ca-Soil (S$_1$)

	Original conc. of Urea (M)	Equilibrium conc. of Urea (M)			Urea adsorbed per 100 gm. of the material (gm.)		
		Ca-Bentonite	Ca-Kaolinite	Ca-Soil (S$_1$)	Ca-Bentonite	Ca-Kaolinite	Ca-Soil (S$_1$)
1.	0·111302	0·10642	0·109837	0·109837	0·0586	0·0116	0·0175
2.	0·065414	0·065414	0·064926	0·065414	nil	0·0058	nil
3.	0·057155	0·05369	0·056627	0·05614	0·0410	0·0058	0·0117
4.	0·035148	0·030754	0·033195	0·034171	0·0527	0·0234	0·0117
5.	0·030266	0·027825	0·025384	0 026847	0·0293	0·0585	0·0410
6.	0·028802	0·020503	0·021967	0·021479	0·0099	0·0820	0·0292

TABLE 3 (a)

Release of Ca^{++} from Ca-bentonite, Ca-Kaolinite and Ca-Soil (S$_1$)

	Concentration of Urea (M)	Vol. of solution used (m.l.)	m.e. of Ca per 100 gm. of the material		
			Ca-Bentonite	Ca-Kaolinite	Ca-Soil (S$_1$)
1.	0·111302	100	57·0	1.4	28·2
2.	0·065414	100	56·6	2·0	28·2
3.	0·057115	100	56·4	1·2	28·4
4.	0·035148	100	56·8	2·4	28·2
5.	0·030266	100	57·6	1·6	28·6
6.	0·028802	100	56·8	2·4	28·4
	Distilled water	100	56·8	Traces.	28·4

TABLE 3 (b)

Release of Ca^{++} from Bentonite (original)

	Concentration of Urea (M)	Vol. of solution used (m.l.)	m. e. Ca per 100 gm. of the material.
1.	0·104956	100	5·4
2.	0·059723	100	4·4
3.	0·045887	100	4·8
4.	0·025384	100	3·4
5.	0·015133	100	3·2
6.	0·010739	100	3·3
	Distilled water	100	3·6

DISCUSSION

From table 1(a), it is clear that in the case of bentonite the adsorption of urea is practically equal for all the concentrations of urea, but in soil, S_1, at higher concentration, no adsorption of urea takes place. Soil, S_2 (Table 1 (d)), which is rich in organic matter and calcium content, also behaves like bentonite. Kaolinite shows a similar trend but at higher concentrations of urea, the adsorption becomes zero. The oxides of iron and aluminium behave like bentonite towards the adsorption of urea at all concentrations.

The adsorption of urea when expressed as percentage of the urea solution added is very interesting. From dilute solutions of urea, practically 50% of the added urea is adsorbed while at highest concentrations, the adsorption does not exceed 10%.

The conversion of bentonite and soil, S_1, to calcium bentonite or Ca-soil, does not appear to bring any remarkable change in the trend of urea-adsorption. The amounts of calcium given out (vide table 3) also do not reflect any increase in them. Practically equal amounts of calcium are liberated from calcium-bentonite and Ca-soil (S_1), when they are treated with urea solutions of different concentrations or with water alone. Thus it is quite clear that more calcium does not pass into solution on the application of urea to soils rich in calcium. Indirectly, it shows that the conversion of urea to ammonium has not taken place during 24 hours.

The above findings indicate that the soils may vary in their abilities to adsorb urea according to their chemical compositions. As the clay minerals like bentonite, kaolinite and the oxides of iron and aluminium have been found to

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possess comparatively high capacities to adsorb urea, their proportions in the soil will greatly determine the capacities to adsorb urea. The organic matter of the soils may also play an important role in increasing the adsorptive capacities of the soils because more urea is adsorbed by the soil S_2 than S_1 (which contains less of carbon).

The results also indicate that the leaching losses of unadsorbed urea from the soils of even wet regions can greatly be minimised by the application of urea in very small doses because more than 50% of the added urea is adsorbed by the soils at very low concentrations of urea.

Further experiments are in progress to find out the retention of urea by soils and clay minerals and on the transformations of the adsorbed urea.

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DETECTION OF RADIOACTIVE FALL-OUT

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ABSTRACT

Methods of detection and estimation of radioactive fall-out and dating the nuclear explosion have been discussed.

The study of the effects of radioactive fall-outs has interested the scientists all over the world ever since the first atomic bomb was exploded. With the increase in number of explosions of atomic and thermonuclear weapons, more attention is being paid to the study of fall-out because of the growing concern over the established ill-effects of the radioaction contamination. For a correct assessment of the harm, that it can cause, it is very essential to measure the quantity of the fall-out brought down to the earth. Air and rainwaters have been chiefly subjected to such measurements in different part of the world. It was thought worthwhile to make measurements at this place, situated far away from the centres of explosions. In this note we will describe the methods which have been generally adopted in such measurements in addition to the observations carried out at Gulmarg.

A. *Radioactivity measurements in Rainwater* :

The general practice is to collect a certain amount of atmospheric precipitation and gradually concentrate it by boiling. The concentrated sample is put aside for two to three days so that the natural radioactive substances, most of which are the daughter products of radon and thoron, may decay to negligible levels.

For measuring beta activity of the concentrated sample, it is dried. Yamasaki and Kaneko (1955) have used infrared lamp for drying the sample in a stainless steel dish. The the measurements of β-activity are made by means of an end-window G. M. Counter of known efficiency.

Sait Akpinar (1957) has followed the method of making the sample by filtering the precipitation through cotton. The cotton is dried and then burnt. The residue, after being allowed to stay for two days, is subjected to measurements by means of a beta-counter shielded by means of 4 inches thick lead.

Another method can be of Auto-radiographing the sample prepared in the above mentioned method. Then by comparison with some standard source, rough estimation of the intensity of radioactive contents can be made. Chief advantage of this method will be that a permanent record is obtained. Of course, the dating of explosion cannot be done by it.

A simple method of studying the gamma-activity in the rainwater was described by Sud and Gill (1958). A thin walled Geiger counter with aquadag cathode has been used. The counter is surrounded by a glass jacket, in which the sample to be

TABLE II

Year	Date	Disintegrations/min./litre.
1959	29th April	3250
do.	30th April	1110
do.	6th May	3050

Comparing our results with that of Terentiuk (1958) we see that the fall-out gets scattered all over the world and that too quite quickly, because around the middle of June, 1956, both his and our records show a sharp increase in contamination. Further in July, 1956, the increases in radioactivity are rather small.

Behounek (1958) has suggested another method for detection and assessment of surface radioactive contamination by means of recording the rate of discharged of a charged conductor.

B. Radioactivity in Atmosphere :

All the above mentioned type of measurements are dependent on the whims of nature while atmospheric air holds a better scope for keeping a regular and continuous record of radioactive contents and its day to day variation in the atmosphere. The usual way is to suck air at a constant rate through a filter. A high volume air sampler is employed for this purpose. Suction may, preferably be done for 24 hours per filter. The filter, then is kept aside for two to three days. After that, the gross beta activity is measured from the filter by means of an end window Geiger counter. Terentiuk (1958) has reported the results of such measurements.

C. Estimation of radioactivity :

Knowing the background counting rate and that with the sample, it is possible to make an estimation of the total radioactive contents present per litre of rain-water or air. Sud & Gill (1958) have calculated the disintegrations per minute per litre of rainwater by multiplying the number of counts, which are in excess over the background, by the efficiency and geometric factors of the counter and the sample containing jacket. By multiplying the disintegrations per minute per litre by $4 \cdot 5 \times 10^{-13}$ the amount of radioactivity in terms of curies per litre can be obtained. Terentiuk (1958) has estimated the radioactive contents of the atmosphere by finding the detection efficiency of the counter, the collection efficiency of the filter and combining the two efficiencies with the excess counts over the background.

D. Dating the nuclear explosion :

The decay curves of the radioactive fall-outs have been commonly used by various workers for dating the nuclear explosions. It is well known that the gross activity of the fall-out follows the law.

$$I_t = I_0 \, t^{-n}$$

Where I_0 is the initial intensity of the fall-out. It is dependent on the initial number of fissions and is a constant. I_t is the gross activity t days after the explo-

tested is poured, thereby making it a 4π counter. Diameter of the counter is 1·5 cm. and the inner diameter of the jacket is 2·5 cm. The counter is kept in the vertical position. The efficiency of the counter for gamma rays has been estimated to be 1 percent.

Measurements were made during June & July in 1956, June to September in 1957 and from January to June in 1958. Some of the rains showed the presence of radioactivity while others did not. Results for those rains which gave an increase in counting rate are given in table 1. The disintegrations per minute per litre was calculated by multiplying the number of counts, which are in excess over the back-ground, by the efficiency and the surface factors of the counter.

TABLE 1

Year	Date	Disintegrations/min./litre
1956	11th June	3535
do.	2nd July	1620
do.	3rd July	1620
1957	9th & 10th June	2532
do.	12th June	2000
do.	13th June	3600
do.	17th June	1333
do.	23rd June	4000
do.	26th June	3333
do.	13th July	6466
do.	25th & 26th August	1000
do.	5th September	1293
do.	7th September	1866
1958	18th June	1333

We are also measuring β-activity in atmospheric precipitation following the method of Yamasaki et al (1955). The diameter of the β-counter is 1·2 cm and that of the dish, used to dry the sample is 1·5 cm. The efficiency of the counter has been estimated as 5% and the surface factor comes out to be 2·5. The results of some measurements are given is table II.

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sion and n is a constant. Different values of n, ranging from 0·9 to 1·5 have been reported. Yamasaki and Kaneko (1955) have given a rather lengthy but simple graphical method for determining both n and the date of explosion. The principle is that suppose the explosion occurs on date T_0 and the measurements on the sample are made on dates T_1 and T_2, giving activity I_1 and I_2 . Then

$$I_1 = I_0\, t_1{}^{-n} \qquad \qquad \text{...} \qquad (1)$$

$$I_2 = I_0\, t_2{}^{-n} \qquad \qquad \text{...} \qquad (2)$$

where $t_1 = T_1 - T_0$ and $t_2 = T_2 - T_0$

From equation (1) and (2) we get,

$$(t_2 - t_1) = \left\{\, (I_1/I_2)^{1/n} - 1 \,\right\} t_1$$

Or $(T_2 - T_1) = (k^{1/n} - 1)\,(T_1 - T_0)$ $\qquad$ ... $\qquad$ (3)

where $\dfrac{I_1}{I_2}$ has been put equal to k,

Similarly if we find another date T_3 on which the intensity T_3 is such that $I_2/I_3 = k$ then we get

$$(T_3) - T_2 = (k^{1/n} - 1)\,(T_3 - T_0) \ldots \ldots \ldots (4)$$

From equations (3) and (4), n and T_0 the only unknowns, can be evaluated.

In order to do it graphically, the sample is measured from time to time and the activity is plotted as a function of date on a semilogrithmic scale.

Let the intensities I_1 and I_2 on dates T_1 and T_2 be such that $\dfrac{I_1}{I_2} = k$, an arbitrarily

chosen constant. Let $T_2 - T_1 = \tau$

same process is repeated and τ', τ'' ; ......are found corresponding to date T_1, T_2; T_1'', T_2'' ; ....

such that $\dfrac{I_1'}{I_2'}$, $\dfrac{I_1''}{I_2''}$ .... are equal to k.

Now if τ, τ', τ'',.....................are plotted as a function of T_1 , T_1', T_1''............... a straight line is obtained.

Its slope will be equal to $(k^{1/n} - 1)$ and the intercept on the T axis will give T_0 , the date of explosion.

Sait Akpinar (1957) has proposed a quicker method for dating the explosion. He makes use of the fact that the beta absorption curves of the fall-out show a continuous change is energy distribution. A quantity α called 'age index' has been defined as $\alpha = \log I_A - \log I_B$ where I_A and I_B are the counting rates with A and B mg/cm² for A & B respectively. He has used 10 and 30 mg/cm² for A & B respectively. With 16 samples collected at different times during 1954-56, a graph has been plotted between Age Index and 'Age'. By 'Age' is meant the time elapsed between the day

of explosion and the day of measurement. With the help of this curve and the counting rates of any sample with 10 and 30 mg cm² absorber, it is possible to assign a date to an unannounced explosion.

It is tacitly assumed in both the methods that the fall-out is due to only one explosion. However, it makes a small difference when two explosions are far removed but the results may be erroneous if the rain has been preceded by two or more nearly spaced explosions.

We are thankful to Mr. Ajit Singh, glass blower, for constructing the counters.

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ON THE DERIVATIVE OF A SELF RECIPROCAL FUNCTION

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1. The object of this short note is to find out certain formulae for the Derivative of a Self Reciprocal Function. We denote a function $f(x)$ as R_μ, if it is Self Reciprocal for Hankel Transforms of order μ, so that it is given by

$$f(x) = \int_0^\infty \mathcal{J}_\mu(xy)\, f(y)\, \sqrt{xy}\, dy, \qquad (1.1)$$

where $J_\mu(x)$ is a Bessel Function of order. For $\mu = 1/2$ and $-1/2$ $f(x)$ is denoted by R_s and R_c respectively.

2. Macrobert (1) has shown that

$$\frac{d}{dx}\, x^{\alpha_1}\, {}_pF_q\left(\begin{array}{c}\alpha_r\;;\, P_s\;;\, \pm x\end{array}\right) = \alpha_1 x^{\alpha_1-1}\, {}_pF_q\left(\begin{array}{c}\alpha_1+1,\, \alpha_2,\, \dots\, \alpha_p\;;\, \pm x\\ P_1\, P_2,\, \dots\, P_q\;;\end{array}\right)$$

$$(2.1)$$

Putting $x^2/2$ for x and simplifying a little, we obtain that

$$\frac{d}{dx}\, x^{2\alpha_1}\, {}_pF_q\left(\begin{array}{c}\alpha_r\;;\, P_s\;;\, \pm\dfrac{x^2}{2}\end{array}\right) = 2\alpha_1 x^{2\alpha_1-1}\, {}_pF_q\left(\begin{array}{c}\alpha_1+1,\, \alpha_2,\dots\alpha_p\;;\, \pm\dfrac{x^2}{2}\\ P_1\, P_2,\, \dots\, P_q\;;\end{array}\right),$$

so that

$$\frac{d}{dx}\, x^{\alpha_1+\frac{1}{2}} \cdot x^{\alpha_1-\frac{1}{2}}\, {}_pF_q\left(\begin{array}{c}\alpha_r\;;\, P_s\;;\, \dfrac{-x^2}{2}\end{array}\right) = \frac{2\alpha_1 x^{\alpha_1+\frac{1}{2}}}{x^{3/2-\alpha_1}}$$

$$x\, {}_pF_q\left(\begin{array}{c}\alpha_1+1,\, \alpha_2,\dots\alpha_p\;;\, \dfrac{-x^2}{2}\\ P_1\, P_2,\dots P_q\;;\end{array}\right)$$

Now let $p=q$. And further let

$$\alpha_2 = \frac{\alpha_1+m_1+1}{2}, \quad \alpha_3 = \frac{\alpha_1+m_2+1}{2}, \quad \dots\dots\dots\dots\dots \quad \alpha_q = \frac{\alpha_1+m_{q-1}+1}{2};$$

and $\quad P_1 = \frac{\alpha_1-m_1+1}{2}, \quad P_2 = \frac{\alpha_1-m_2+1}{2}, \quad \dots\dots\dots\dots\dots \quad P_q = \frac{\alpha_1+v+1}{2}.$

Then we obtain that

$$\frac{d}{dx}\left\{ x^{\alpha_1+\frac{1}{2}} \cdot x^{\alpha_1-\frac{1}{2}} \; {}_qF_q\left(x_1, \frac{\alpha_1+m_1+1}{2}, \frac{\alpha_1+m_2+1}{2}, \frac{\alpha_1-m_1+1}{2}, \frac{\alpha_1-m_2+1}{2}, \right.\right.$$

$$\left.\left. \ldots\ldots \alpha_q = \frac{\alpha_1+m_{q-1}+1}{2}; \frac{\alpha_1+\nu+1}{2}; \frac{-x^2}{2} \right)\right.$$

$$= \frac{2\alpha \cdot x^{\alpha_1+\frac{1}{3}}}{x^{3/2-\alpha_1}} \; {}_qF_q\left(\alpha_1+1, \frac{\alpha_1+m_1+1}{2}, \ldots\ldots \frac{\alpha_1+m_{q-1}+1}{2}; \frac{-x^2}{2} \right) \quad (2.2)$$

Dineshchandra (2) has shown that the function

$$x^{\alpha_1-\frac{1}{2}} \; {}_qF_q\left(\alpha_1, \frac{\alpha_1+m_1+1}{2}, \ldots\ldots \frac{\alpha_1+m_{q-1}+1}{2} \atop \frac{\alpha_1-m_1+1}{2}, \ldots\ldots \frac{\alpha_1-m_{q-1}+1}{2}, \frac{\alpha_1+\nu+1}{2}; - \frac{x^2}{2} \right) \quad (2.3)$$

is $\pm R_\nu$ according as $m_1+m_2+ \ldots\ldots +m_{q-1}$ is an even or odd integer, where m_1, m_2, m_3, m_4, ... are all positive integers. Hence from (2.2) and (2.3) we find that the function

$$\frac{1}{x^{3/2-\alpha_1}} \cdot x^{\alpha_1+\frac{1}{2}} \; {}_qF_q\left(\alpha_1+1, \frac{\alpha_1+m_1+1}{2}, \ldots\ldots \frac{\alpha_1+m_{q-1}+1}{2}; \atop \frac{\alpha_1-m_1+1}{2}, \ldots\ldots \frac{\alpha_1+\nu+1}{2}; - \frac{x_2}{2} \right) \quad (2.4)$$

is the derivative of $x^{\alpha_1+\frac{1}{2}}$ times the R_ν function given in (2.3).

3. Particular Cases of this function are interesting. Let

$$m_1 = m_2 = \ldots\ldots\ldots m_n = 0$$

Then we obtain that

$$\frac{d}{dx}\left\{ x^{\alpha_1+\frac{1}{2}} \cdot x^{\alpha_1-\frac{1}{2}} \; {}_1F_1\left(\alpha_1; \frac{\alpha_1+\nu+1}{2}; \frac{-x_2}{2} \right) \right.$$

$$= \frac{2\alpha_1}{x^{3/2-\alpha_1}} \; x^{\alpha_1+\frac{1}{2}} \left(\alpha_1+1; \frac{\alpha_1+\nu+1}{2}; \frac{-x^2}{2} \right) \quad (3.1)$$

Now, putting $m_1 = m_2 = \ldots\ldots = m_{q-1} = 0$ in (2.3) we find that

$$x^{\alpha_1-\frac{1}{2}} \; {}_1F_1\left(\alpha_1; \frac{\alpha_1+\nu+1}{2}; \frac{-x^2}{2} \right), \quad (3.2)$$

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is R_v while the function

$$x^{\alpha_1+\frac{1}{2}}\ {}_1F_1\left(\alpha_1+1;\ \frac{\alpha_1+v+1}{2};\ \frac{-x^2}{2}\right)$$

(3.3)

is R_{v-1}. Hence, from (3.2), 3.3) and (3.1) we find that

$$\frac{d}{dx}\left\{x^{\alpha+\frac{1}{2}}\ R_v\ \text{function}\right\}=x^{\alpha-3/2}\ R_{v-1}\ \text{function}$$

(3.4)

In particular, putting $\alpha=3/2$ we then obtain that

$$\frac{d}{dx}\left(x^2.\,R_v\ \text{function}\right)=R_{v-1}\ \text{function}$$

(3.5)

4. Again, let $\alpha+1=\dfrac{\alpha+v+1}{2}$

so that $\alpha=v-1$.

Then the equation (2.2) may be written as

$$\frac{d}{dx}\left\{x^{v-\frac{1}{2}}\ x^{v-3/2}\ {}_qF_q\left(\begin{matrix}v-1,\ \frac{v+m_1}{2},\ \ldots\ldots\ldots\ \frac{v+m_{q-1}}{2};\\ \frac{v-m_1}{2},\ldots\ldots\ldots\ldots\ldots\ v\ ;\end{matrix}\ \frac{-x^2}{2}\right)\right\}$$

$$=\frac{2\alpha\,x^{v-3/2}}{x^{3/2-v}}\ {}_qF_q\left(\begin{matrix}v-1,\ \frac{v+m_1,}{2},\ \ldots\ldots\ldots\ldots\ \frac{v+m_{q-1}}{2};\\ \frac{v-m_1}{2},\ \frac{v-m_2}{2},\ldots\ldots\ldots\ldots\ v-1\ ;\end{matrix}\ \frac{-x^2}{2}\right)$$

(4.1)

Comparing (4.1) with (2.3) we find that

$$x^{v-3/2}\ {}_qF_q\left(\begin{matrix}v-1_1\ \frac{v+m_1}{2},\ \ldots\ldots\ldots\ldots\ldots\ \frac{v+m_{q-1}}{2};\\ \frac{v-m_1}{2},\ \ldots\ldots\ldots\ldots\ldots\ldots\ v\ ;\end{matrix}\ \frac{-x^2}{2}\right),$$

(4.2)

is R_v.

While the function

$$x^{v-3,2}\ {}_qF_q\left(\begin{matrix}v-1_1\ \frac{+m_1}{2},\ \frac{v+m_2}{2},\ \ldots\ldots\ldots\ldots\ \frac{v+m_{q-1}}{2};\\ \frac{v-m_1}{2},\ \ldots\ldots\ldots\ldots\ldots\ldots\ v-1\ ;\end{matrix}\ \frac{-x^2}{2}\right),$$

(4.3)

is R_{v-2}

Hence from (4.1), (4.2) and (4.3) we conclude that

$$\frac{d}{dx}\left(x^{v-1/2}\ R_v \text{ function }\right) = K\ x^{v-3/2}\ R_{v-2} \text{ function.} \tag{4.4}$$

where $\alpha_1 = v - 1$ and K is a certain constant.

In particular, putting $v = 3/2$, we obtain that

$$\frac{d}{dx}\left\{x\ R_v \text{ function }\right\} = K\ R_{v-2} \text{ function.} \tag{4.5}$$

It should be noted that the formula (3.4) is valid when α_1 and v are independent of each other, while (4.4) is valid only if $\alpha_1 = v - 1$.

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HYPERSURFACES OF A KAEHLER MANIFOLD

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ABSTRACT

In this paper it has been shown that (i) the necessary and sufficient condition that a geodesic in a Kaehler manifold should be a geodesic in its hypersurface also is that it should both be a geodesic and an asymptotic line on the hypersurface as in the case of a Riemannian manifold ; (ii) if two hypersurfaces of a Kaehler manifold intersect along a curve and if the curve is a line of curvature on both the hypersurfaces, then the hypersurfaces intersect at a constant angle along the curve. Some other properties of hypersurfaces of a Kaehler manifold have also been obtained.

1. Introduction :

[1] The metric of a Hermitian manifold is given by

$$ds^2 = 2g_{\alpha\bar{\beta}} \, dz^{\alpha} \, dz^{\bar{\beta}} \qquad \ldots (1.1)$$

If the tensor $g_{\alpha\bar{\beta}}$ also satisfies the condition

$$\frac{\partial g_{\alpha\bar{\beta}}}{\partial z^{\bar{\gamma}}} = \frac{\partial g_{\alpha\bar{\gamma}}}{\partial z^{\bar{\beta}}} \qquad \ldots (1.2)$$

[2] (which is known as Kaehler's condition), then the complex manifold with metric (1·1) satisfying the condition (1·2) is called a Kaehler manifold. We shall denote such a manifold by V^c_n (or V^r_{2n}).

The Christoffel symbols of a Kaehler manifold are given by

$$\overline{\begin{matrix} \alpha \\ \beta\gamma \end{matrix}} = g^{\alpha\bar{\varepsilon}} \frac{\partial g_{\bar{\varepsilon}\beta}}{\partial z^{\gamma}} \qquad \ldots (1.3)$$

$$\overline{\begin{matrix} \bar{\alpha} \\ \bar{\beta}\bar{\gamma} \end{matrix}} = g^{\bar{\alpha}\varepsilon} \frac{\partial g}{\partial z^{\bar{\gamma}}}$$

The only non vanishing components of the Riemann curvature tensor are

$$R^{\alpha}_{\beta\gamma\bar{\delta}} \quad , \quad R^{\bar{\alpha}}_{\bar{\beta}\bar{\gamma}\delta} \qquad \text{and these are given by}$$

$$R^{\alpha}_{\beta\gamma\bar{\delta}} = \frac{\partial \overline{\begin{matrix} \alpha \\ \beta\gamma \end{matrix}}}{\partial z^{\bar{\delta}}} , \quad R^{\bar{\alpha}}_{\bar{\beta}\bar{\gamma}\delta} = \frac{\partial \overline{\begin{matrix} \bar{\alpha} \\ \bar{\beta}\bar{\gamma} \end{matrix}}}{\partial z^{\delta}} \qquad \ldots (1.4)$$

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It follows that the only non-vanishing component of the Riemann tensor of the first kind is $R_{\alpha\bar{\beta}\gamma\delta}$

and that it is given by

$$R_{\alpha\bar{\beta}\gamma\delta} = -g_{\alpha\varepsilon}\frac{\partial\Gamma^{\bar{\varepsilon}}_{\bar{\beta}\delta}}{\partial z^{\gamma}} = -g_{\bar{\beta}\varepsilon}\frac{\partial\Gamma^{\varepsilon}_{\alpha\gamma}}{\partial z^{\delta}} \quad \ldots \quad (1.5)$$

Since the metric of a Kaehler manifold is given by

$$ds^2 = 2g_{\alpha\bar{\beta}}\, dz^{\alpha}\, dz^{\bar{\beta}}\,,$$

'ds' can be interpreted as magnitude of displacement vector. Therefore the magnitude V of a vector whose components are $(v^{\alpha}, v^{\bar{\alpha}})$ is defined by $V^2 = 2g_{\alpha\bar{\beta}}\, v^{\alpha}\, v^{\bar{\beta}}$.

If there are two self adjoint vectors whose components are $(u^{\alpha}, u^{\bar{\alpha}})$ and $\left(v^{\alpha}, v^{\bar{\alpha}}\right)$ then the scalar $g_{\alpha\bar{\beta}}\, u^{\alpha}\, v^{\bar{\beta}}$ is a complex quantity and we write $re^{i\theta} = g_{\alpha\bar{\beta}}\, u^{\alpha}\, v^{\bar{\beta}}$ \quad\quad $\ldots$ (1.6)

From the property of self adjointness it follows that $re^{-i\theta} = g_{\bar{\alpha}\beta}\, u^{\bar{\alpha}}\, v^{\beta}$ \quad (1.7)

Here 'θ' is interpreted as the angle between the two vectors.

Adding (1.6) and (1.7) we get $2r\cos\theta = g_{\alpha\bar{\beta}}\, u^{\alpha}\, v^{\bar{\beta}} + g_{\bar{\alpha}\beta}\, u^{\bar{\alpha}}\, v^{\beta}$ and multiplying them we get $r^2 = \left(g_{\alpha\bar{\beta}}\, u^{\alpha}\, v^{\bar{\beta}}\right)\left(g_{\bar{\alpha}\beta}\, u^{\bar{\alpha}}\, v^{\beta}\right)$.

It follows that

$$\cos\theta = \frac{g_{\alpha\bar{\beta}}\, u^{\alpha}\, v^{\bar{\beta}} + g_{\bar{\alpha}\beta}\, u^{\bar{\alpha}}\, v^{\beta}}{2\sqrt{g_{\alpha\bar{\beta}}\, u^{\alpha}\, v^{\bar{\beta}}}\,\sqrt{g_{\bar{\alpha}\beta}\, u^{\bar{\alpha}}\, v^{\bar{\beta}}}} \quad \ldots \quad (1.8)$$

2. Hypersurfaces of a Kaehler Manifold :

Let there be a Kaehler manifold of complex dimensions n and real dimensions $2n$ with coordinates $\left(z^{\alpha}, z^{\bar{\alpha}}\right)$.

Let ϕ be a complex analytic function of z's then the equations

$$\phi(z^1, z^2, \ldots, z^n) = c$$
$$\bar{\phi}(z^{\bar{1}}, z^{\bar{2}}, \ldots, z^{\bar{n}}) = \bar{c} \quad \ldots \quad (2.1)$$

[. 171]

represent a hypersurface of the manifold, for the variety represented by (2·1) will be of complex dimensions $(n-1)$ and real dimensions $2(n-1)$.

[3] It has already been shown that a hypersurface of Kaehler manifold is also a Kaehler manifold.

The normal to the hypersurface at the point $(z^a, z^{\bar{a}})$ has components

$$\left(\frac{\partial \phi}{\partial z^a} , \frac{\partial \bar{\phi}}{\partial z^{\bar{a}}} \right)$$

for by differentiating (2.1) totally we get

$$\frac{\partial \phi}{\partial z^a} dz^a = 0 ,$$

$$\frac{\partial \bar{\phi}}{\partial z^{\bar{a}}} dz^{\bar{a}} = 0 ,$$

$\left(dz^a , dz^{\bar{a}} \right)$ being components of a vector tangential to the hypersurface.

Let now there be a manifold of complex dimensions $(n+1)$ and real dimensions $2(n+1)$ and a hypersurface V^c_n of complex dimensions n and real dimensions $2n$ immersed in that Kaehler manifold.

Also let $\left(\xi^a , \xi^{\bar{a}} \right)$ be the complex coordinates of any point in the Kaehler manifold V^c_{n+1} and $\left(z^i , z^{\bar{i}} \right)$ the complex coordinates of that point in the hyper-surface.

In what follows Greek indices will take the values $\left(\begin{matrix} 1, & 2, & \ldots\ldots & , & n+1 \\ \bar{1}, & \bar{2}, & \ldots\ldots & , & \overline{n+1} \end{matrix} \right)$ and Latin indices will take the values $\left(\begin{matrix} 1, & 2, & \ldots\ldots & , & n \\ \bar{1}, & \bar{2}, & \ldots\ldots & , & \bar{n} \end{matrix} \right)$

Here ξ's are complex analytic functions of z's.

Let $a_{\alpha\bar{\beta}}$ be the fundamental tensor for V^c_{n+1} and $g_{i\bar{j}}$ be the fundamental tensor of V^c_n. Then the metrics of V^c_{n+1} and V^c_n are respectively

$$ds^2 = 2a_{\alpha\bar{\beta}} \, d\xi^\alpha \, d\xi^{\bar{\beta}}$$

$$ds^2 = 2g_{i\bar{j}} \, dz^i \, dz^{\bar{j}}$$

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Since the infinitesimal distance between two points which lie both in $V^c{}_n$ and $V^c{}_{n+1}$ is invariant, we have

$$g_{i\bar{j}} \, dz^i \, dz^{\bar{j}} = a_{\alpha\bar{\beta}} \, d\xi^\alpha \, d\xi^{\bar{\beta}}$$

Since ξ's are complex analytic functions of z's

$$\therefore \quad \frac{\partial \xi^\alpha}{\partial z^{\bar{i}}} = 0$$

and thus $d\xi^\alpha = \dfrac{\partial \xi^\alpha}{\partial z^i} \, dz^i$

Similarly $d\xi^{\bar{\beta}} = \dfrac{\partial \xi^{\bar{\beta}}}{\partial z^{\bar{i}}} \, dz^{\bar{i}}$

$$\therefore \quad g_{i\bar{j}} \, dz^i \, dz^{\bar{j}} = a_{\alpha\bar{\beta}} \, \frac{\partial \xi^\alpha}{\partial z^i} \, dz^i \, \frac{\partial \xi^{\bar{\beta}}}{\partial z^{\bar{j}}} \, dz^{\bar{j}}$$

or $\qquad g_{i\bar{j}} = a_{\alpha\bar{\beta}} \, \dfrac{\partial \xi^\alpha}{\partial z^i} , \quad \dfrac{\partial \xi^{\bar{\beta}}}{\partial z^{\bar{j}}}$ $\qquad \qquad$ ... (2.2)

Let $\overline{\left|\begin{smallmatrix} \alpha \\ \beta\gamma \end{smallmatrix}\right|}$ and $\left\{\begin{smallmatrix} i \\ jk \end{smallmatrix}\right\}$ be the Christoffel symbols of the second kind formed with respect to $a_{\alpha\bar{\beta}}$ and $g_{i\bar{j}}$ respectively, satisfying Kaehler conditions.

Then $\left\{\begin{smallmatrix} i \\ jk \end{smallmatrix}\right\} = g^{i\bar{h}} \, \dfrac{\partial g_{j\bar{h}}}{\partial z^k}$

$$\overline{\left|\begin{smallmatrix} \alpha \\ \beta\gamma \end{smallmatrix}\right|} = g^{\alpha\bar{\varepsilon}} \, \frac{\partial g_{\bar{\varepsilon}\beta}}{\partial z^\gamma}$$

For a fixed α, ξ's are invariant functions of z's

$$\therefore \quad \frac{\partial \xi^\alpha}{\partial z^i} = \xi^\alpha_{,i}$$

$$= \xi^\alpha_{;i}$$

and $\dfrac{\partial \xi^{\bar{\alpha}}}{\partial z^{\bar{i}}} = \xi^{\bar{\alpha}}_{,\bar{i}} = \xi^{\bar{\alpha}}_{;\bar{i}}$

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where a comma followed by an index denotes the covariant derivative w. r. t. the co-ordinate having that index and a semicolon followed by an index denotes the tensor derivative with respect to the co-ordinate having that index.

$$\text{i. e.,} \quad u^i,_j = \frac{\partial u^i}{\partial z^j} + \left\{ \begin{matrix} i \\ jk \end{matrix} \right\} u^k$$

$$\zeta^a_{;j} = \frac{\partial \zeta^a}{\partial \xi^\beta} \frac{\partial \xi^\beta}{\partial z^j} + \overline{\left[\begin{matrix} a \\ \beta\gamma \end{matrix}\right.} \zeta^\beta \frac{\partial \xi^\gamma}{\partial z^j}$$

Let $(N^a, N^{\bar{a}})$ be the componets of unit normal vector to the hypersurface

$$\text{then} \quad 2a_{a\bar{\beta}} \ N^a N^{\bar{\beta}} = 1 \qquad \qquad \text{... (2,3)}$$

and since $\xi^a_{,i}$ regarded as a vector in V^c_{n+1} is tangential to the hypersurface

$$\therefore \quad a_{a\bar{\beta}} \ N^a \xi^{\bar{\beta}},_{\bar{j}} = 0, \ a_{a\bar{\beta}} \ N^{\bar{\beta}} \xi^a,_i = 0 \left.\begin{matrix} \\ \\ \end{matrix}\right\}$$

$$\text{Also} \quad a_{a\bar{\beta}} \ N^a N^{\bar{\beta}},_{\bar{j}} = 0 \qquad \qquad \text{... (2.4)}$$

Since ξ's are complex analytic functions of z's

$$\text{we have} \quad \xi^a_{;\,i\bar{j}} = 0, \ \xi^{\bar{a}}_{;\,\bar{i}j} = 0$$

Taking the tensor derivative of (2.2)

$$\text{we get} \quad a_{a\bar{\beta}} \ \xi^a_{;\,ik} \xi^{\bar{\beta}},_{\bar{j}} = 0$$

i. e. $\left(\xi^a_{;\,ik}, 0 \right)$ regarded as a vector in V^c_{n+1} is orthogonal to $\left(0, \xi^{\bar{a}}_{,\bar{i}} \right)$ (regarded as a vector in V^c_{n+1}) which is tangential to the hypersurface, or $\left(\xi^a_{;\,i}, 0 \right)$ regarded as a vector in V^c_{n+1} is normal to the hypersurface.

$$\therefore \quad \text{We can write} \quad \xi^a_{;\,ij} = \Omega_{ij} N^a \qquad \qquad \text{... (2.5)}$$

$$\text{Similarly} \quad \xi^{\bar{a}}_{;\,\bar{i}\bar{j}} = \Omega_{\bar{i}\bar{j}} N^{\bar{a}}$$

It follows that $\quad \Omega_{i\bar{j}} = 0$

$$\Omega_{\bar{i}j} = 0$$

3. Curvature of a curve in a hypersurface.

We know that if (U^a, $U^{\bar{a}}$) are components of a self adjoint vector in V^c_{n+1} and (u^i, $u^{\bar{i}}$) are components of the same vector in V^c_n, then

$$U^a = \xi^a{}_{,i}\, u^i$$

$$U^{\bar{a}} = \xi^{\bar{a}}{}_{,\bar{i}}\, u^{\bar{i}}$$

Taking the tensor derivative of each side of the first equation, we get

$$U^a{}_{;j} = \xi^a{}_{;ij}\, u^i + \xi^a{}_{;i}\, u^i{}_{,j}$$

Multiplying by $\dfrac{dz^j}{ds}$ and substituting from (2·5) we obtain

$$U^a{}_{;j}\frac{dz^j}{ds} = \left(\Omega_{ij}\, u^i\, \frac{dz^j}{ds}\right) N^a + \xi^a{}_{;i}\, u^i\, \frac{dz^j}{ds}$$

and a similar expression for $U^{\bar{a}}{}_{;\bar{j}}\dfrac{dz^{\bar{j}}}{ds}$

If the vector (U^a, $U^{\bar{a}}$) is tangent to the curve, then $u^i = \dfrac{dz^i}{ds}$ and we get

$$q^a = \left(\Omega_{ij}\,\frac{dz^i}{ds}\frac{dz^j}{ds}\right) N^a + \xi^a{}_{;i}\, p^i$$

$$q^{\bar{a}} = \left(\Omega_{\bar{i}\bar{j}}\,\frac{dz^{\bar{i}}}{ds}\frac{dz^{\bar{j}}}{ds}\right) N^{\bar{a}} + \xi^{\bar{a}}{}_{;\bar{i}}\, p^{\bar{i}} \qquad\qquad ...(3.1)$$

where (q^a, $q^{\bar{a}}$) are the components of the first curvature vector of the curve in V^c_{n+1} and (p^i, $p^{\bar{i}}$) are its components V^c_n.

$$\text{Let} \qquad \Omega_{ij}\,\frac{dz^i}{ds}\frac{dz^j}{ds} = K_n$$

$$\Omega_{\bar{i}\bar{j}}\,\frac{dz^{\bar{i}}}{ds}\frac{dz^{\bar{j}}}{ds} = \overline{K}_n$$

We shall define $|K_n|$ (modulus of K_n) as the normal curvature of the curve. $|K_n|$ is the magnitude of the vector whose components are ($K_n N^\alpha$, $\overline{K}_n N^{\bar{a}}$), for ($N^a$, $N^{\bar{a}}$) is a unit vector. The vector ($K_n N^a$, $\overline{K}_n N^{\bar{a}}$) is the normal curvature vector. Since (K_n, $\overline{K}_n$) depends upon the direction of the curve at that point,

we can also call $|K_n|$ as normal curvature of the complex hypersurface V^c_n at the point for the direction of the curve.

4. Conjugate and Asymptotic directions in the hypersurface of the Kaehler manifold :

Two directions given by unit vectors whose components are (u^i, $u^{\bar{i}}$) and (v^i, $v^{\bar{i}}$) are defined to be conjugate with respect to the hypersurface,

if
$$\Omega_{ij}\, u^i\, v^j = 0$$

$$\Omega_{\bar{i}\bar{j}}\, u^{\bar{i}}\, v^{\bar{j}} = 0$$

A direction which is self conjugate is said to be asymptotic.

If the direction given by (u^i, $u^{\bar{i}}$) is asymptotic, then we must have

$$\Omega_{ij}\, u^i\, u^j = 0$$

$$\Omega_{\bar{i}\bar{j}}\, u^{\bar{i}}\, u^{\bar{j}} = 0$$

An asymptotic line is a curve on the hypersurface, the direction of which at every point is asymptotic.

The differential equations of the asymptotic lines are

$$\Omega_{ij}\, dz^i\, dz^j = 0$$

$$\Omega_{\bar{i}\bar{j}}\, dz^{\bar{i}}\, dz^{\bar{j}} = 0 \qquad \ldots \text{(4.1)}$$

If we take the square of the magnitude of the vector (q^a, $q^{\bar{a}}$) given by (3.1) we obtain

$$K_a{}^2 = |K_n|^2 + Kg^2 \qquad \ldots \text{(4.2)}$$

where Ka is the curvature of the curve in V^c_{n+1}
and Kg is the curvature of the curve in V^c_n.

Kg is also known as geodesic curvature of the curve.

It is clear that geodesic curvature of the curve is zero for the gedesics on the hypersurface.

From (4.2) it follows that the necessary and sufficient conditions that Ka is zero, are $|K_n| = 0$ and Kg = 0. The necessary and sufficient condition that a geodesic in a Kaehler manifold should be a geodesic in its hypersurface also is that it should both be a geodesic and an asymptotic line on the hypersurface, as in the case of a Riemannian manifold.

5. Derived vector of unit normal to a hypersurface :

Taking tensor derivative of (2.3) we obtain

$$a_{\alpha\bar{\beta}} N^\alpha{}_{;\, i}\, N^{\bar{\beta}} + a_{\alpha\bar{\beta}}\, N^\alpha\, N^{\bar{\beta}}{}_{;\, i} = 0 \qquad \ldots \text{(5.1)}$$

This shows that $(N^{\bar{\alpha}}_{;1}, N^{\bar{\alpha}}_{;1})$ regarded as a vector in $V^{\bar{\epsilon}}_{n+1}$ is orthogonal to the normal vector $(N^{\alpha}, N^{\bar{\alpha}})$.

The components $(N^{\alpha}_{;1} N^{\bar{\alpha}}_{;1})$ are expressible as

$$N^{\alpha}_{;1} = A^{k}_{1} \xi^{\alpha}_{;k}$$

$$N^{\bar{\alpha}}_{;1} = A^{\bar{k}}_{1} \xi^{\bar{\alpha}}_{;\bar{k}} \qquad \qquad \dots \quad (5\cdot2)$$

Taking the tensor derivative of the second equation of (2·4) we obtain

$$a_{\alpha\bar{\beta}} \; \xi^{\alpha}_{;ij} N^{\bar{\beta}} + a_{\alpha\bar{\beta}} \; \xi^{\alpha}_{;1} N^{\bar{\beta}}_{;j} = 0$$

Substituting from (2·5) and (5·2), we get

$$\Omega_{ij} + a_{\alpha\bar{\beta}} \; \xi^{\alpha}_{;1} \xi^{\bar{\beta}}_{;\bar{k}} A^{\bar{k}}_{j} = 0$$

$$\therefore \Omega_{ij} = - g_{1\bar{k}} A^{\bar{k}}_{j}$$

Multiplying both sides by $g^{i\bar{h}}$ and summing on i

we get $\qquad \Omega_{ij} g^{i\bar{h}} = - A^{\bar{h}}_{j}$

Similarly we shall obtain

$$\Omega_{\bar{i}\bar{j}} g^{\bar{i}h} = - A^{h}_{j}$$

$\therefore$ We get $\qquad N^{\bar{\alpha}}_{;i} = - \Omega_{ij} g^{j\bar{k}} \xi^{\bar{\alpha}}_{;\bar{k}}$

and similarly $N^{\alpha}_{;\bar{i}} = - \Omega_{\bar{i}\bar{j}} g^{\bar{j}k} \xi^{\alpha}_{;k}$

and since $\Omega_{i\bar{j}} = 0$, $g^{ik} = 0$ and $\xi^{\alpha}_{;\bar{k}} = 0$

$$N^{\alpha}_{;i} = 0$$

Similarly $N^{\bar{\alpha}}_{;\bar{i}} = 0$

Hence we get the result that the vectors whose components are $\left(N^{\alpha}_{;\bar{i}}, N^{\bar{\alpha}}_{;j} \right)$ form a null vector field in $V^{\bar{\epsilon}}_{n+1}$, for if m is the magnitude of such a vector.

then $m^2 \equiv 2 a_{\alpha\bar{\beta}} N^{\alpha}_{;i} N^{\bar{\beta}}_{;\bar{j}} = 0$

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By a similar argument we can show that vectors whose component are $\left(N^a_{;i}, N^{\bar{\alpha}}_{;i} \right)$ form a null vector field in V^c_{n+1}.

It should be noticed that the vectors whose component are $\left(N^a_{;i}, N^{\bar{\alpha}}_{;i} \right)$ and $\left(N^a_{;\bar{i}}, N^{\bar{\alpha}}_{;\bar{i}} \right)$ are different vectors in V^c_{n+1}.

Now derived vectors of unit normal in the direction of unit vector $\left(u^i, u^{\bar{i}} \right)$ have components $\left(N^a_{;\bar{i}} u^{\bar{i}}, N^{\bar{\alpha}}_{;i} u^i \right)$

where $N^a_{;\bar{j}} u^{\bar{i}} = - u^{\bar{i}} \Omega_{\bar{i}\bar{j}} g^{\bar{j}k} \xi^a_{;k}$

and $N^{\bar{\alpha}}_{;i} u^i = - u^i \Omega_{ij} g^{j\bar{k}} \xi^{\bar{\alpha}}_{;\bar{k}}$

If $(a^i, a^{\bar{i}})$ are components of any other unit vector tangential to the hypersurface, then its components in V^c_{n+1} are $\left(\xi^a_{;i} a^i, \xi^{\bar{\alpha}}_{;\bar{i}} a^{\bar{i}} \right)$, and the resolved part of the derived vector of unit normal in the direction of this vector

is given by $-\left(u^{\bar{i}} \Omega_{\bar{i}\bar{j}} g^{\bar{j}k} \xi^\alpha_{;k} \right) a_{\alpha\bar{\beta}} \left(\xi^{\bar{\beta}}_{;\bar{i}} a^{\bar{i}} \right)$ and its conjugate

or $- u^{\bar{i}} \Omega_{\bar{i}\bar{j}} g^{\bar{j}k} g_{k\bar{i}} a^{\bar{i}}$ and its conjugate.

or $- \Omega_{\bar{i}\bar{j}} u^{\bar{i}} a^{\bar{j}}$ and its conjugate.

If this expression vanishes then the directions of vectors u and a are conjugate.

Hence conjugate directions in the hypersurface of a Kaehler manifold are such that the derived vector of unit normal in either direction is orthogonal to the other direction.

In a particular case, in which direction is self conjugate we may state that the derived vector of unit normal along a curve is orthogonal to the curve, if the curve is an asymptotic line in the hypersurface, as in the case of Riemannian manifolds.

If the direction of derived vector of (N^a, $N^{\bar{\alpha}}$) in the direction of vector $(u^a, u^{\bar{\alpha}})$ is identical with that of (U^a, $U^{\bar{\alpha}}$),

then $u^{\bar{i}} \Omega_{\bar{i}\bar{j}} g^{\bar{j}k} \xi^a_{;k} = w\, u^l \xi^a_{;l}$

$u^i \Omega_{ij} g^{j\bar{k}} \xi^{\bar{\alpha}}_{;\bar{k}} = \bar{w}\, u^{\bar{l}} \xi^{\bar{\alpha}}_{;\bar{l}}$

where w is scalar function.

Multiplying first of these equations by $a_{\alpha\bar{\beta}}\ \xi^{\bar{\beta}}_{;\,h}$ we get

$$u^{\bar{i}}\,\Omega_{i\bar{h}} = w\,g_{j\bar{h}}\,u^{j}$$

or $$u^{\bar{i}}\,\Omega_{i\bar{h}} - w\,g_{j\bar{h}}\,u^{j} = 0$$

Similarly $$u^{i}\,\Omega_{\bar{i}h} - \overline{w}\,g_{\bar{j}h}\,u^{\bar{j}} = 0$$

These equations show that vector u is a principal direction of the hypersurface.

Hence the derived vector of unit normal with respect to V^{c}_{n+1} will be tangential to the curve, if the curve is a line of curvature of the hypersurface.

6. Generalised Equations of Gauss & Codazzi for Kaehler Manifold.

By applying Ricci's identities to $\xi^{a}_{,\,i}$ (regarded as covariant vector in V^{c}_{n}) we have $\xi^{a}_{,\,ij\bar{k}} - \xi^{a}_{,\,i\bar{k}j} = \xi^{a}_{,\,p}\ g^{p\bar{h}}\,R_{i\bar{h}j\bar{k}}$

and since $$\xi^{a}_{;\,j\bar{k}} = 0,$$

$$\xi^{a}_{,\,ij\bar{k}} = \xi^{a}_{,\,p}\ g^{p\bar{h}}\,R_{i\bar{h}j\bar{k}} \qquad \ldots (6.1)$$

Also we have

$$\Omega_{ij}\cdot N^{a} \equiv \xi^{a}_{;\,ij} = \xi^{a}_{,\,ij} + \overline{}^{a}_{\beta\gamma}\ \xi^{\beta}_{;\,i}\ \xi^{\gamma}_{;\,j} \qquad \ldots (6.2)$$

Taking the tensor derivative of (6.2) and substituting from (6.1) we get

$$\Omega_{ij;\,\bar{k}} + \Omega_{ij}\,N^{a}_{;\,\bar{k}} = \xi^{a}_{,\,p}\ g^{p\bar{h}}\,R_{i\bar{h}j\bar{k}} + R'^{a}_{\beta\gamma\delta}\ \xi^{\beta}_{,\,i}\ \xi^{\gamma}_{,\,j}\ \xi^{\bar{\delta}}_{,\,\bar{k}}$$

Where $R'^{a}_{\beta\gamma\delta}$ is Riemamn tensor of the second kind formed with respect to $\overline{}^{a}_{\beta\gamma}$

Substituting for $N^{a}_{;\,\bar{k}}$ from (5.3), we get

$$\left(R_{i\bar{h}j\bar{k}} - \Omega_{ij}\,\Omega_{\bar{h}\bar{k}}\right) g^{p\bar{h}}\,\xi^{a}_{;\,p} = \Omega_{ij;\,\bar{k}}\,N^{a} - R'^{a}_{\beta\gamma\delta}\ \xi^{\beta}_{,\,i}\ \xi^{\gamma}_{,\,j}\ \xi^{\bar{\delta}}_{,\,\bar{k}} \qquad (6.3)$$

Multiplying (6.3) by $a_{a\bar{\varepsilon}}\ \xi^{\bar{\varepsilon}}_{,\,\bar{l}}$ we shall get

$$R_{i\bar{l}j\bar{k}} = \Omega_{ij}\,\Omega_{\bar{l}\bar{k}} + R'_{\beta\bar{\varepsilon}\gamma\delta}\ \xi^{\beta}_{,\,i}\ \xi^{\bar{\varepsilon}}_{,\,\bar{l}}\ \xi^{\gamma}_{,\,j}\ \xi^{\bar{\delta}}_{,\,\bar{k}} \qquad \ldots (6.4)$$

which is Gauss's equation for a Kaehler manifold.

Multiplying (6.3) by $a_{a\bar{\varepsilon}}$ $N^{\bar{\varepsilon}}$ we get

$$\Omega_{ij;\bar{k}} = R'_{\bar{\varepsilon}\beta\gamma\delta}\, \xi^{\beta}_{,\,i}\, \xi^{\gamma}_{,\,j}\, \xi^{\bar{\delta}}_{,\,\bar{k}}\, N^{\bar{\varepsilon}} \qquad\qquad ...(6.5)$$

Similarly we obtain $\Omega_{\bar{i}\bar{j};k} = R'_{\varepsilon\bar{\beta}\bar{\gamma}\delta}\, \xi^{\bar{\beta}}_{,\,\bar{i}}\, \xi^{\bar{\gamma}}_{,\,\bar{j}}\, \xi^{\delta}_{;\,k}\, N^{\varepsilon}$ \qquad ...(6.6)

(6.5), (6.6) are Codazzi's equations for the Kaehler manifold.

7. Now we shall prove an important property of a Kaehler manifold, *viz.*

If two hypersurfaces intersect along a curve and if the curve is a line of curvature on both the hypersurfaces, then the hypersurfaces are inclined at a constant angle along the curve.

Proof :— Let $(M^a, M^{\bar{a}})$ & $(N^a, N^{\bar{a}})$ represent unit normals to the two hypersurfaces. If 'θ' is the angle between the normals at any point of the curve of intersection

then $\qquad \cos\theta = a_{a\bar{\beta}}\, M^a\, N^{\bar{\beta}} + a_{\bar{a}\beta}\, M^{\bar{a}} N^{\beta}$

The intrinsic derivative of $\cos\theta$ in the direction of the curve is

$$a_{a\bar{\beta}} \left(M^a_{;\,\bar{i}}\, \frac{dz^{\bar{i}}}{ds}\, N^{\bar{\beta}} + M^a\, N^{\bar{\beta}}_{,\,j}\, \frac{dz^j}{ds} \right)$$

$$+ a_{\bar{a}\beta} \left(M^{\bar{a}}_{;\,i}\, \frac{dz^i}{ds}\, N^{\beta} + M^{\bar{a}}\, N^{\beta}_{;\,\bar{j}}\, \frac{dz^{\bar{j}}}{ds} \right)$$

But the curve is a line of curvature in both the hypersurfaces,

∴ the derived vectors of unit normals of both hypersurfaces are tangential to the curve.

$$\therefore \quad M^a_{;\,\bar{i}}\, \frac{dz^{\bar{i}}}{ds} = K\, \xi^a_{,\,p}\, \frac{dz^p}{ds}, \quad M^{\bar{a}}_{;\,i}\, \frac{dz^i}{ds} = \bar{K}\, \xi^{\bar{a}}_{,\,p}\, \frac{dz^{\bar{p}}}{ds}$$

and $\qquad N^{\bar{\beta}}_{;\,j}\, \frac{dz^j}{ds} = K'\, \xi^{\bar{\beta}}_{,\,\bar{h}}\, \frac{dz^{\bar{h}}}{ds}, \quad N^{\beta}_{;\,\bar{j}}\, \frac{dz^{\bar{j}}}{ds} = \bar{K}'\, \xi^{\beta}_{,\,h}\, \frac{dz^h}{ds}$

Substituting these values in (7.1) we obtain

$$a_{a\bar{\beta}}\, \xi^a_{,\,p}\, N^{\bar{\beta}} = 0$$

$$a_{\bar{a}\beta}\, \xi^{\beta}_{,\,h}\, M^{\bar{a}} = 0$$

$$a_{a\bar{\beta}}\, \xi^{\bar{\beta}}_{,\,\bar{h}}\, M^a = 0$$

$$a_{a\bar{\beta}}\, \xi^{\bar{\beta}}_{,\,\bar{h}}\, N^a = 0$$

therefore the expression in (7.1) vanishes i. e., the intrinsic derivative of $\cos \theta$ along the curve is zero or θ is constant along the curve.

Hence the hypersurfaces intersect at a constant angle along the curve.

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ANALYSIS AND COMPOSITION OF THE PRODUCTS OBTAINED FROM THE SYSTEMS OF SODIUM-MOLYBDATE WITH MINERAL ACIDS ON AGEING

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ABSTRACT

The deposits obtained in the systems of sodium molybdate with hydrochloric-, nitric-, and sulphuric acids at higher acid concentrations, on ageing, were seperated into water-soluble and water-insoluble portions and these were analysed for water of crystallisation, content of molybdinum trioxide, and content of Na_2O. The analysis had shown that the deposits in all the cases were chiefly mixtures of sodium tetramolybdate and the insoluble molybdic acid. The probable mechanism of the formation of these deposits in different systems is discussed.

Various polymolybdates of different compositions are known to be formed by evaporating a solution of sodium molybdate at different pH values, from a highly alkaline to an acidic range. The present authors, while studying the effect of ageing on the system of sodium molybdate with mineral acids, observed the formation of certain products in highly acid solutions[1,2]. Mostly, they were mixtures of crystalline and amorphous products. These were analysed and probable molecular compositions and formulae are given.

EXPERIMENTAL METHODS

The products obtained at different molybdate/acid ratios in the strongly acid solutions of each system with a mineral acid, were separated into water soluble and water insoluble portions in the following way. About 0·5 gm of the product was treated with 50 c.c. of distilled water and heated on a water-bath with constant stirring. The solution was allowed to settle and filtered through a weighed gooch crucible. The insoluble portion was left in the crucible. The crucible was dried and weighed again with the insoluble part. The difference in weight of the crucible with and without the insoluble portion gave the weight of the insoluble product. The difference in weight of the original product taken and the weight of the insoluble portion gave the weight of the water soluble portion. The original product, water soluble and insoluble portions were analysed for the following :—

(*i*) Water of crystallization in the original product and insoluble portion ;

(*ii*) Percentage of MoO_3 in water soluble and insoluble products ; and

(*iii*) Percentage of sodium if any in the soluble and insoluble portions.

(*i*) *Water of crystallization* :—The substance of a known weight was heated at a emperature between 150°C to 200°C and the loss of weight if any on heating determines the amount of water of crystallization. However, in the insoluble part no loss of weight was observed on heating and hence no water of crystallization is present.

(*ii*) (*a*). *Estimation of MoO₃ and sodium in the water soluble portion* :—The solution containing the water soluble part was acidified with acetic acid and lead acetate was added slowly to the hot solution till the precipitation of lead molybdate (PbMoO₄) was complete. The solution was allowed to settle and filtered through a gooch crucible. The precipitate was washed with 1% solution of ammonium acetate and finally transferred to the gooch, dried and weighed as PbMoO₄. The amount of MoO₃ was obtained by multiplying the amount of PbMoO₄ with the factor 0·39213. The filtrate was concentrated and lead was removed as lead sulphate by precipitating out with dilute H₂SO₄. The filtrate after the removal of molybdenum and lead was concentrated to a very small volume and sodium was estimated as sodium-uranyl-zinc-acetate[3]. The method consists of adding to a concentrated solution of a sodium salt, the reagent zinc uranyl acetate, when a coarse crystalline precipitate of sodium uranyl zinc acetate-(NaC₂H₃O₂.Zn (C₂H₃O₂)₂.3UO₂ (C₂H₃O₂)₂. 6H₂O –is formed. The solution was allowed to stand overnight and filtered through a sintered crucible. The triple acetate precipitate was washed first with a very dilute solution of the reagent, then with alcohol, and finally with acetone. The precipitate was dried at room temperature and weighed. The amount of sodium was obtained by multiplying the amount of sodium zinc-uranyl acetate with the factor 0·01495.

(*ii*) (*b*). *Estimation of MoO₃ and sodium in the water insoluble portion* :—The insoluble portion was treated with ammonium hydroxide when it dissolved. Then the same procedure was adopted for the estimation of MoO₃ and sodium as in the case of the water soluble part.

The results of analyses of the products obtained at molybdate/acid ratios 1:2·5 to 1:5 of the system Na₂MoO₄—HCl on ageing are given in the following tables:—

TABLE I

Analysis for water content

Ratio of Na₂MoO₄ to HCl	Wt. of product taken (gm.)	Weight after heating (gm.)	loss of wt. due to dehydration (gm.)	% of hydration
1:2·5	0·2135	0·1875	0·0260	12·30
1:3	0·2250	0·1972	0·0278	12·34
1:3·5	0·2648	0·2320	0·0328	12·37
1:4	0·2340	0·2051	0·0299	12·35
1:5	0·2210	0·1938	0·0272	12·31

TABLE 2

Analysis for % of water soluble and insoluble portions

Ratio	wt. of product taken (gm.)	wt. of water insoluble (gm.)	wt. of water soluble (gm.)	% of water insoluble	% of water soluble
1 : 2·5	0·5627	0·1790	0·3837	31·80	68·20
1 : 3	0·5426	0·1926	0·3500	35·50	64·50
1 : 3·5	0·5525	0·2088	0·3437	37·80	62·20
1 : 4	0·5565	0·2314	0·3251	41·58	58·42
1 : 4·5	0·5610	0·2504	0·3106	44·65	55·35
1 : 5	0·5412	0·2613	0·2799	47·58	52·42

TABLE 3

Analysis of water soluble part

Ratio	wt. of product in soln. (gm.)	Amount of MoO_3 (gm.)	% of MoO_3	Amount of NaO_2 (gm.)	% of Na_2O
1 : 2·5	0·3837	0·3033	79·05	0·0326	8·49
1 : 3	0·3500	0·2757	78·78	0·0296	8·45
1 : 3·5	0·3437	0·2725	79·25	0·0292	8·50
1 : 4	0·3251	0·2557	78·89	0·0277	8·52
1 : 4·5	0·3106	0·2462	79·30	0·0264	8·48
1 : 5	0·2799	0·2221	79·29	0·0238	8·50

TABLE 4

Analysis of water insoluble part

Ratio	wt. of product (gm.)	Amount of MoO_3 (gm.)	% of MoO_3
1 : 2·5	0·1790	0·1588	88·70
1 : 3	0·1926	0·1707	88·65
1 : 3·5	0·2088	0·1865	88·90
1 : 4	0·2314	0·2051	88·75
1 : 4·5	0·2504	0·2119	88·65
1 : 5	0·2613	0·2321	88·85

Results of the analysis of the products obtained at molybdate/acid ratios 1 : 3 to 1 : 5 of the system $Na_2 MoO_4$—HNO_3 on ageing :—

TABLE 5

Analysis for water content

Ratio	wt. of the product (gm.)	wt. after heating to 200°C (gm.)	loss of wt. due to hydration (gm.)	% of hydration
1 : 3	0·2657	0·2330	0·0327	12·28
1 : 3·5	0·2426	0·2127	0·0299	12·30
1 : 4	0·2354	0·2061	0·0293	12·27
1 : 4·5	0·2567	0·2251	0·0316	12·30
1 : 5	0·2436	0·2748	0·0288	12·32

TABLE 6

Analysis for % of water soluble and insoluble portions ... ...

Ratio	wt. of the product (gm.)	amount of water insoluble (gm.)	Amount of water soluble (gm.)	% of water insoluble	% of water soluble
1 : 3	0·5250	0·1444	0·3806	26·50	70·50
1 : 3·5	0·5213	0·1815	0·3398	34·80	65·20
1 : 4	0·5562	0·2024	0·3538	36·55	53·45
1 : 4·5	0·5529	0·2103	0·3326	38·75	51·25
1 : 5	0·5326	0·2224	0·3102	41·74	58·26

TABLE 7

Analysis of water soluble part

Ratio	Amount in soln (gm.)	Amount of MoO_3 (gm.)	% of MoO_3	Amount of Na_2O (gm.)	% of Na_2O
1 : 3	0·3806	0·3007	79·01	0·0323	8·48
1 : 3·5	0·3398	0·2681	78·85	0·0289	8·49
1 : 4	0·3538	0·2793	78·92	0·0301	8·51
1 : 4·5	0·3326	0·2634	79·20	0·0282	8·47
1 : 5	0·3102	0·2451	78·00	0·0264	8·49

TABLE 8

Analysis of water insoluble part

Ratio	wt. of the product (gm.)	wt. of MoO$_3$ (gm.)	% of MoO$_3$
1 : 3	0·1444	0·1211	88·76
1 : 3·5	0·1815	0·1610	88·82
1 : 4	0·2024	0·1798	88·92
1 : 4·5	0·2103	0·1864	88·65
1 : 5	0·2240	0·1962	88·80

The results of the analysis of the products obtained at ratios 1 : 4 to 1 : 5 of the system $Na_2\text{-}MoO_4$—H_2SO_4 are given below : –

TABLE 9

Analysis for water content

Ratio	wt. of the product (gm.)	wt. after heating (gm.)	loss of weight (gm.)	% of hydration
1 : 4	0·2459	0·2156	0·0303	12·30
1 : 4·5	0·2785	0·2511	0·0274	12·32
1 : 5	0·2653	0·2393	0·0260	12·35

TABLE 10

Analysis for % of water soluble & insoluble parts

Ratio	wt. of the product (gm.)	amount of water insoluble (gm.)	amount of water soluble (gm)	% of water insoluble	% of water soluble
1 : 4	0·5785	0·1780	0·4005	30·75	69·25
1 : 4·5	0·5622	0·1884	0·3741	33·50	66·25
1 : 5	0·5822	0·2244	0·3578	38·55	61·45

TABLE 11

Analysis of water soluble part

Ratio	Amount in solution (gm.)	Content of MoO$_3$ (gm.)	% of MoO$_3$ (gm)	Content of Na$_2$O (gm.)	% of Na$_2$O
1 : 4	0·4005	0·3174	79·25	0·0341	8·50
1 : 4·5	0·3741	0·2962	79·18	0·0317	8·45
1 : 5	0·3578	0·2828	79·20	0·0304	8·48

TABLE 12

Analysis of water insoluble part.

Ratio	Wt. of product (gm.)	Content of MoO_3 (gm.)	% of MoO_3
1 : 4	0·1780	0·1536	89·10
1 : 4·5	0·1894	0·1683	90·30
1 : 5	0·2244	0·2003	89·25

DISCUSSION

The results of analysis of the products obtained on ageing the systems of molybdate with mineral acids show that (i) the percentage of water of crystallization of all the products in all the systems is nearly the same ; (ii) the water insoluble portion of the products increases with the increase in ratio of molybate to acid ; (iii) the percentage of MoO_3 and sodium content of the watersoluble part and the percentage of MoO_3 of the insoluble portion are also the same in all the products obtained from different systems. In the table below against each item of anaylysis and under each system, only the mean values of the results of analysis of the products obtained at various molybdate/acid ratios are given. The high values of MoO_3 content in the case of the system Na_2MoO_4-H_2SO_4 are due to the adhered SO_4^{--} ions to the products which also form insoluble $PbSO_4$ precipitate along with $PbMoO_4$ when molybdenum is precipitated with lead acetate as lead molybdate.

TABLE 13

No.	Item of analysis	Systems in which the products are obtained on ageing			
		Na_2MoO_4 and HCl	Na_2MoO_4 and HNO_3	Na_2MoO_4 and H_2SO_4	mean values
		%	%	%	
1.	Water of crystallization in the original product.	12·33	12·29	12·32	12·32
2.	Water of crystallization in insoluble portion	nil	nil	nil	nil
3.	Content of MoO_3 in the water soluble portion	79·0	78·98	79·21	79·06
4.	Content of Na_2O in the water soluble portion	88·75	88·71	89·75	89·07
5.	Content of Na_2O in the water soluble portion	8·48	8·49	8·48	8·48
6.	Content of Na_2O in the insoluble portion.	nil	nil	nil	nil

From the above table it is evident that the water of crystallization found in the original product is due to the water soluble portion only, as the insoluble portion does not contain any. The water soluble portion also contains sodium whereas it is absent in the case of the insoluble portion. Therefore, is clear that the soluble part is a sodium molybdate, possibly a polymolybdate whereas the insoluble portion is a simple or polymolybdic acid. It is found that the observed composition of the water soluble portion very nearly agrees with sodium tetramolybdate with five molecules of water of crystallization, ($Na_2Mo_4O_{13}$. $5H_2O$). The observed mean and calculated compositions for the tetramolybdate-pentahydrate are given below:—

		observed mean values	calcualted values
1.	Water of crystallization	12·36%	12·31%
2.	Content of MoO_3	79·12%	79·062%
3.	Content of Na_2O	8·51%	8 48%

Ullik[4] prepared sodium tetramolybdate and formulated the product with $5\frac{1}{2}$ molecules of water of crystallization-$Na_2MoO_4O_{13}.5\frac{1}{2}H_2O$. A. Rosenheim and J. Felix[5] obtained a crystalline hexahydrate which they represented as $Na_2\ Mo_4\ O_{13}$ $6H_2O$. But the product analysed in the present work shows to have only 5 molecules of the water of crystallization. The variable quantity of water shows the instability of the salt when dried, losing its hydration.

In some samples, the water soluble portion made up to the volumes so as to give the cencentration N/256 with respect to the amount of $Na_2\ Mo_4O_{13}$ present in solution. It was not possible to prepare solutions of higher concentrations like N/32, N/64 or N/128 as the water soluble portions do not contain the required amount of the salt. Moreover, the amounts of products obtained on ageing were only limited. The specific conductivity of N/256, N512 and N/1024 solution was measured at 25° from which the equivalent conductivity was calculated. These results show below are nearly in agreement with the equivalent conductivity of the sodium tetramolybdate as measured by Rosenheim and Felix[5] various dilution.

Dilution in litres	Equivalent conductivity	
	Observed by Rosenheim & Felix	Observed by the authors
256	130·4	138·25
512	145·0	145·95
1024	162·8	173·55

The higher equivalent conductivity in our results might be due to the very slightly soluble aged molybdic acid passing into the portion of water soluble of the original products during the separation of the insoluble.

Further our conductivity results of the solutions containing water soluble portions show that the tetramolybdate separated on ageing is only a normal salt, but

not the hydrogen salt in which case the conductivity results should have been comparatively higher.

The mean values of the results given in Table 13 show that the insoluble portions of different products analysed do not contain sodium or water of crystallization. The mean MoO_3 content i.e. $89^.07\%$ corresponds to that of the simple molybdic acid, the calculated value of which comes to $88^.89$. Therefore, the insoluble portion is only molybdic acid H_2MoO_4. Now it can be calculated on the basis of the analysis that all the products obtained in different systems on ageing are only mixtures of sodium tetramolybdate and molybdic acid. The probable mechanism of the formation of precipitations in the different systems is discussed below :—

(1) $Na_2MoO_4 - HCl$:—It was shown earlier[1] that in the case of this system the aggregation goes on till the ratio 1:2 resulting in the formation of a tetramolybdate which is decomposed to form acid tetramolybdate at various ratios higher than 1:2. The insoluble products are obtained only after the ratio 1:2 and therefore it is the acid tetramolybdate which undergoes changes on ageing with the precipitation of sodium tetramolybdate and molybdic acid. The change may be explained by the following reaction :—

$$2NaHMo_4O_{13} \text{------} Na_2Mo_4O_{13} + H_2Mo_4O_{13}$$
$$H_2Mo_4O_{13} + 3H_2O \text{------} \rightarrow 4H_2MoO_4.$$
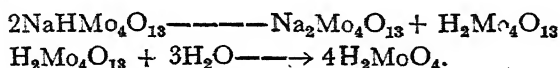
(2) $Na_2MoO_3 - HNO_3$:—In this case aggregation goes on till the ratio 1:3 when the hexamolybdate is formed, which undergoes decomposition at higher ratios with the formation of an acid hexamolybdate[1]. The precipitates were formed in this system after the ratio 1:3. Thereafter the acid hexamolybdate undergoes hydrolysis on ageing with the liberation of tetramolybdate and molybdic acid. The reactions explaining the probable changes may be stated as :—

$$2 NaHMo_6O_{19} + H_2O \rightarrow Na_2Mo_4O_{13} + 2H_2Mo_4O_{13}$$
$$H_2Mo_4O_{13} + 3H_2O \rightarrow 4H_2MoO_4.$$
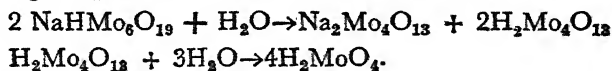
(3) $Na_2MoO_4 - H_2SO_4$:—In this system the aggregation takes place between 1:2 and 1:4 ratios, which results in the formation of a tetramolybdate[2]. The precipitates are obtained in this system from the ratio 1:4 only. No evidence was obtained here for the formation of an acid tetramolybdate. As the products obtained on ageing were shown to be tetramolybdate and molybdic acid on analysis. The formation of molybdic acid is due to the action on the tetramolybdate of the sulphuric acid which is present in excess in the system. The hydrolysis of the tetramolybdate leading to the liberation of insoluble molybdic acid on ageing, may be explained by the following reactions :—

$$Na_2Mo_4O_{13} + H_2SO_4 \rightarrow H_2Mo_4O_{13} + Na_2SO_4$$
$$H_2Mo_4O_{13} + 3H_2O \rightarrow 4H_2MoO_4.$$
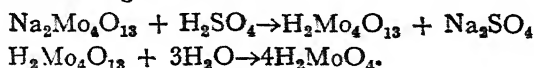
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CHEMICAL EXAMINATION OF *MATTHIOLA INCANA*
(RED VARIETY)

PART II—STUDY ON OIL

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Matthiola incana (red variety) also known as *Lipedium iberis* (Hindi and Punjabi-Lal Towdri) belonging to N. O. *Cruciferae* is cultivated in Indian gardens, indigenous in Mediterranean regions and Western Europe. It also extends from Southern Europe to Siberia. It is a well-known medicinal plant and is used by Ayurvedic physicians as aphrodisiac and in purifying blood. The medicinal properties of the seeds resemble closely to those of white and yellow varieties.

Matthiola incana (seeds red Variety) has been subjected to a systematic chemical examination. The seed was tested for the organic and inorganic substances. On complete incineration, the powdered seeds gave 9·2% ash of which 46·2% was water-soluble and 53·8% was acid-soluble. The ash on analysis was found to contain sodium, potassium, iron, calcium and magnesium as basic radicals and chloride, sulphate, carbonate and silicate as acid radicals.

Preliminary chemical examination of the seeds showed the presence of an oil, mucilage[1] and a mixture of colouring matters. The alkaloids, glucosides, saponins, free reducing sugars, tannins and free organic acids were found to be absent.

The complete chemical study of the oil revealed that erucic (41·42%), oleic (20·81%) and linoleic acids (26·24%) were present as major components, the characteristic feature of the oils obtained from crucifereous seeds while palmitic (4·74%) stearic (1·61%) and linolenic acids (5·18%) were present as minor components in the mixed acid fraction. The unsaponifiable matter consists of phytosterols and sitosterol.

CHEMICAL EXAMINATION OF THE OIL

Five thousand grams of the powdered seeds were exhaustively extracted with petroleum ether (b. p. 40 – 60°C). The petroleum ether was filtered hot and the filtrate was kept overnight. No solid substance settled down on keeping. From the petroleum-ether extract the crude oil was obtained and purified (yield – 8·2%). The crude oil was purified by animal charcoal and Fuller's earth.

The pure oil has the following physical and chemical constants :—

Sp. Gr. (30°C), 0·9149; Ref. Index (30°C), 1·4332; Acid Value, 19·2, Sap. value, 186·6; Iodine Value, 110·2 and unsaponifiable matter, 0·92%.

Two hundred and ten grams of the pure oil were completely saponified with alcoholic caustic potash. From the completely saponified oil, the unsaponifiable

matter and mixed fatty acids were separated. The ether extraction of the soap gave 0·92% unsaponifiable matter and the ether extraction of the decomposed soap gave 82·24% of mixed fatty acids. The iodine value (Hanus) of the mixture was found to be 122·2. The freshly extracted mixed acids were in liquid form but on keeping for a long time they solidified.

The mixed fatty acids were then separated into solid and liquid fractions by the Twitchell's lead salt alcoholic process modified by Hilditch and co-workers[2]. The percentage and chemical constants of the solid and liquid acid-fractions are given below :—

TABLE 1

No.	Fraction		Percentage	Iodine Value
1.	Solid acid fraction	...	46·22	66·5
2.	Liquid acid fraction	...	53·78	139·2

QUANTITATIVE ESTIMATION OF LIQUID ACIDS

The estimation of the liquid acids were carried out by two methods, bromination and methyl-ester methods :

(A) *Bromination method* :— 10 gms. of the acid from the liquid-acid fraction were estimated by dissolving the acid in ether (at – 10°C) and brominated according to the method of Eibner and Muggenthaler[3], modified by Jamieson and Boughmann[4]. The results are given below :—

TABLE 2

S. No.	Acids		Percentage in mixed acid
1.	Oleic	...	18·49
2.	Linolenic	...	5·16
3.	Linoleic	...	26·30

The unsaturated acids were also estimated by methyl-ester method. The unsaturated fatty acids were converted into the corresponding methyl esters by refluxing the acid mixture with absolute methyl alcohol in presence of sulphuric acid in the usual manner. The dried methyl-ester mixture (20·22 g) was fractionated under reduced pressure. The amount of individual fraction collected, at various temperatures and pressure (5 m.m.) is given in Table 3.

[191]

TABLE 3

Fraction	Temp. range	Wt. of distillate in gms.
l_1	Upto 190°C	7·4960
l_2	190 – 195°C	7·9236
l_3	195 – 200°C	2·3344
l_4	200 – 205°C	1·5104
l_5	Above 205°C	0·7248
	Loss in distillation	0·2308

Saponification and iodine values of each fraction were determined. From these values, the amount of various acids in different fractions were calculated out by Jamieson and Boughmann method.[5]

The calculated values of the fatty acids, in liquid acid fraction and in the mixed acids are given below :—

TABLE 4

Acids		Percentage in liquid acid fraction	Percentage in mixed acid fraction
Palmitic	...	0·22	0·12
Oleic	...	34·06	18·34
Linoleic	...	48·52	26·24
Linolenic	...	9·54	5·18
Erucic	...	7·66	3·90

EXAMINATION OF THE SOLID ACIDS

The solid acids were converted into methyl esters. 20·1899g of the esters were distilled fractionally at reduced pressure (5 m.m.) and the results of the distillation are given below :—

TABLE 5

Fraction	Temp. range	Wt. of the distillate in gms
S_1	170 – 175°C	0·2210
S_2	175 – 180°C	0·8856
S_3	180 – 185°C	2·0196
S_4	185 – 190°C	3·9712
S_5	Above 190°C	12·9010
	Loss during distillation	0·1915

The different fractions obtained were analysed and percentage of various acids in solid acid and mixed acid fractions were calculated according to the method of Jamieson and Boughmann[5]. The results obtained are given below :—

TABLE 6

Acid		Percentage in solid acid fraction	Percentage in mixed acid fraction
Palmitic	...	9·98	4·62
Stearic	...	3·41	1·61
Oleic	...	5·28	2·47
Erucic	...	81·33	37·52

The constituent fatty acids of each fraction were identified by hydrolysing each fraction separately and the liberated acids were crystallised repeatedly from alcohol-acetone mixture. The pure sample of the acids thus obtained were identified by determining their melting points with the authentic samples of the corresponding acids. The saturated fatty acids present, were palmitic and stearic acids.

The total percentage of the various fatty acids of the oil, in mixed, solid and liquid fatty acid fractions are given below :—

TABLE 7

Acids		Solid acid fraction	Liquid acid fraction	Mixed acid fraction
Palmitic	...	9·98	0·22	4·74
Stearic	...	3·41	...	1·61
Erucic	...	81·33	7·66	41·42
Oleic	...	5·28	34·06	20·81
Linoleic	...	...	48·52	26·24
Linolenic	...	...	9·54	5·18

The unsaponifiable matter was obtained by extracting the soap solution with ether. The yield was 0·92%. It was a semi-solid yellowish mass. It was purified by treating with petroleum ether and finally recrystallised with alcohol. The pure compound responded positively to all the colour tests for sterols. A sterol was isolated from the mixture. It melted at 137°C and its acetyl derivative melted at 127-28°C. It was inferred to be sitosterol.

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EFFECT OF CALCIUM-PHOSPHATES, ROCK PHOSPHATE AND BASIC SLAG ON LOSS OF NITROGEN FROM AMMONIUM SULPHATE WHEN ADDED TO SOIL ALONG WITH ORGANIC MATTER

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ABSTRACT

The loss of nitrogen from ammonium sulphate when applied to soil is decreased markedly by addition of different phosphates like mono-calcium phosphate, di-calcium phosphate, tri-calcium phosphate, basic slag and rock phosphate when added along with organic matter.

It is well known that the recovery of nitrogen from artificial fertilizers usually remains below 50% (1, 2, 3). Dhar (4) has emphasized the value of phosphates in the fixation of atmospheric nitrogen and in preventing the loss from artificials when applied along with organic matter. The present study comprises the effect of different phosphates when added to ammonium sulphate in different doses to soils along with organic matter.

EXPERIMENTAL

The soil used for this experiment was collected from the fields infront of Sheila Dhar Institute of Soil Sciences, University of Allahabad, India. The soil under study was light grey to brownish black in colour and alluvial in origin. Normal crops are grown on it. Its chemical composition was determined by the methods recommended by Piper (5) and A. O. A. C. (6). Top nine inches of soil was collected and passed through a 100 mesh sieve after air-drying. An amount of oven dried soil was taken to which when organic matter in the form of cow-dung and/or different phosphates were added, the total weight of the reacting mixture became 200 gms. Five different phosphates *viz.* mono-calciumphosphate, di-calcium phosphate, tri-calcium phosphate, rock phosphate and basic slag were added as 0.5% P_2O_5. The cow-dung was added as 0.5% carbon. The reacting mixture was taken in 24 cm diameter enamel dishes. Nitrogen was added at the rate of 43 lbs., 86 lbs. and 129 lbs. per acre as ammonium sulphate. The mixture was stirred on alternate days to make it homogenous and the moisture content was maintained at 20-25% by adding distilled water. This was kept in the laboratory at 27°C and samples were analysed after definite intervals for total carbon (7) and total nitrogen (8, 9).

The results obtained are recorded below :—

TABLE 1

Percentage composition of the soil used

Silica (HCl insoluble)	78·401
Loss on ignition	2·103
Sesquioxide	11·375
Silica/sesquioxide ratio	13·6
Fe_2O_3	4·520
CaO	3·318
MgO	1·640
K_2O	1·470
Total P_2O_5	0·219
Available P_2O_5	0·038
(1% citric acid soluble)	
Al_2O_3	6·855
Exchangeable Calcium	6·66 m.e. %
Total carbon	0·1527
Total nitrogen	0·0347
C/N ratio	4·4
Ammoniacal nitrogen	0·002
Nitrate nitrogen	0·001
Total available nitrogen	0·004
Total/available nitrogen	8·0

TABLE 2

Percentage composition of cow-dung used

Loss on ignition	63·460
Ash	36·530
Silica	30·660
CaO	2·520
MgO	0·934
K_2O	0·721
P_2O_5	0·673
Total carbon	28·6300
Total nitrogen	1·0108
C/N ratio	28·34

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TABLE 3

Analysis of Rock phosphate and Basic slag

	Rock phosphate	Basic slag
Silica	6·300%	23·660%
CaO	20·800%	34·360%
MgO	1·920%	5·280%
Fe_2O_3	4·200%	11·720%
Al_2O_3	26·900%	......
K_2O	......	9·070%
Total P_2O_5	27·800	7·590%
Available P_2O_5	1·000	4·460%
(1% Citric acid soluble)		

TABLE 4

Effect of phosphates on loss of nitrogen from ammonium sulphate when added at the rate of 43 lbs of Nitrogen per acre to the soil

	% loss of N at the end of 60 days	% loss of N at the end of 120 days
Soil + carbon as cow dung + ammonium sulphate	20·1	39·9
Soil + carbon as cow dung + ammonium sulphate + mono-calcium phosphate	16·9	36·9
Soil + carbon as cow dung + ammonium sulphate + di-calcium phosphate	15·0	34·8
Soil + carbon as cow dung + ammonium sulphate + tri-calcium phosphate	16·0	35·7
Soil + carbon as cow dung + ammonium sulphate + Basic slag	16·2	35·9
Soil + carbon as cow dung + ammonium sulphate + Rock phosphate	16·7	36·4

TABLE 5

Effect of phosphates on loss of nitrogen from ammonium sulphate when added at the rate of 86 lbs of nitrogen per acre to the soil

	% loss of N after 60 days	% loss of N after 120 days
Soil + carbon as cow dung + ammonium sulphate	22·2	41·2
Soil + carbon as cow dung + ammonium sulphate + mono-calcium phosphate	19·3	38·3
Soil + carbon as cow dung + ammonium sulphate + di-calcium phosphate	17·1	36·1
Soil + carbon as cow dung + ammonium sulphate + tri-calcium phosphate	18·0	37·2
Soil + carbon as cow dung + ammonium sulphate + Basic slag	18·3	37·5
Soil + carbon as cow dung + ammonium sulphate + Rock phosphate	18·9	38·0

TABLE 6

Effect of phosphates on loss of nitrogen from ammonium sulphate when added at the rate of 129 lbs nitrogen per acre to the soil

	% loss of N after 60 days	% loss of N after 120 days
Soil + carbon as cow dung + ammonium sulphate	24·6	44·5
Soil + carbon as cow dung + ammonium sulphate + mono-calcium phosphate	21·3	41·8
Soil + carbon as cow dung + ammonium sulphate + di-calcium phosphate	19·4	39·4
Soil + carbon as cow dung + ammonium sulphate + tri-calcium phosphate	20·3	40·5
Soil + carbon as cow dung + ammonium sulphate + Basic slag	20·6	40·9
Soil + carbon as cow dung + ammonium sulphate + Rock phosphate	21·0	41·5

DISCUSSION

The above observations show that a part of the nitrogen added as sulphate of ammonia is lost with lapse of time. The % loss of nitrogen increases with increasing doses of nitrogen. The loss is more marked at the end of 120 days than at the end of 60 days.

The effect of the addition of different phosphates along with organic matter in the form of cow dung is that they minimise the loss of nitrogen from ammonium sulphate when applied to soil. Their efficiency in checking the loss of nitrogen from ammonium sulphate is in the following order : —

Di-calcium phosphate > Tri-calcium phosphate > Basic slag > Rock phosphate Mono calcium phosphate

It appears that the addition of various phosphates is helpful in the fixation of atmospheric nitrogen in the soil in presence of organic matter in the form of cow dung. Thus nitrogen loss and nitrogen gain go on side by side in the soil. The total nitrogen determinations that have been made measures only the balance of nitrogen loss and nitrogen gain. So the net result appears to be a retarding effect on the loss of nitrogen from ammonium sulphate, when organic matter is added along with different phosphates to the soil (10, 11).

Phosphates may also effect in checking the loss of nitrogen in ways other than described above. They may help in stabilising the proteins of the soils. The proteins that are present in soil humus are likely to be stabilised by the formation of nucleo-proteins, phospho-proteins'or other substances (12). These more stable protein complexes seem to resist ammonification and nitrification better than proteins alone and thus the loss of nitrogen decreases.

More-over calcium ions introduced along with these phosphates may react with unstable substance ammonium nitrite (which is formed as a result of nitrification) and form calcium nitrite which is more stable than ammonium nitrite and thus retard the loss of nitrogen from ammonium sulphate.

Also the decomposition of ammonium nitrite is accelerated by acids. When organic matter undergoes oxidation some of the organic acids are produced in the system which accelerate the decomposition of ammonium nitrite leading to the loss of nitrogen. But in presence of phosphates which act as buffer the increase in H-ion concentration of the system is not possible and so this also retards the loss of nitrogen by decreasing the docomposition of ammonium nitrite.

Hence over-all effect of addition of phosphates is that they minimise the loss of nitrogen considerably.

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ON SOME PROPERTIES OF K-TRANSFORM INVOLVING MEIJER'S G-FUNCTION

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1. **Introduction** :—A function $\phi(p)$ defined by

$$(1.1) \quad \phi(p) = p \int_0^\infty e^{-px} f(x)\, dx, \quad R(p) > 0$$

is called the Laplace Transform of $f(x)$ which is called its original. Meijer (5) gave a generalization of this in the form

$$(1.2) \quad \psi(p) = \sqrt{\frac{2}{\pi}} \cdot p \int_0^\infty (px)^{\frac{1}{2}} K_\nu(px) f(x)\, dx, \quad R(p) > 0$$

Since $\quad K_{\pm\frac{1}{2}}(x) = \left(\frac{\pi}{2x}\right)^{\frac{1}{2}} e^{-x}$

(1.2) reduces to (1.1) when $\nu = \pm\frac{1}{2}$.

$\psi(p)$ is called the Meijer Transform (also known as the K-Transform) of order ν and $f(x)$ its original in this transform.

We shall represent (1.2) symbolically as

$$\psi(p) \; \frac{k}{\nu} \; f(x)$$

while (1.1) shall be denoted as usual by

$$\phi(p) \doteqdot f(x)$$

In this paper we shall obtain two theorems connecting any two functions $\psi(p)$ and $g(x)$ through a chain of symbolic relations in this transform and then shall utilize the theorems to evaluate certain infinite integrals involving product of Meijer's G-Function with the Bessel and hyper-geometric functions and with the G-Function itself.

Roopnarain (6) has obtained similar theorems in respect of the generalized Laplace transform defined by R. S. Varma (8).

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2. Theorem 1.

If $\psi(p) \overset{k}{\underset{\lambda}{=\!=\!=}} f(x)$

and $p^{-l-\frac{1}{2}} f\left(\dfrac{1}{p}\right) \overset{k}{\underset{\mu}{=\!=\!=}} g(x)$

then

$$\psi(p) = \frac{2^{-l-3/2}}{\pi} \, p^{l+3/2} \int\limits_0^\infty G_{0,\,4}^{4,\,0}\left(\frac{p^2 x^2}{16}\,\bigg|\,\frac{1}{4}+\frac{\mu}{2},\frac{1}{4}-\frac{\mu}{2},\frac{\lambda-l}{2},\frac{-\lambda-l}{2}\right) g(x)\, dx$$

provided the integral involved is convergent.

Proof: The Parseval-Goldstein theorem (1) can be generalized in respect of K-Transform and can be stated thus :

If $\phi_1(b) \overset{k}{\underset{v}{=\!=\!=}} f_1(x)$

and
$\phi_2(p) \overset{k}{\underset{v}{=\!=\!=}} f_2(x)$

then

$$(2.1) \quad \int\limits_0^\infty \phi_1(x)\, f_2(x)\, \frac{dx}{x} = \int\limits_0^\infty \phi_2(x)\, f_1(x)\, \frac{dx}{x}$$

Applying this theorem to (4, p. 147)

$$x^{l-1} k_\lambda\left(\frac{a}{x}\right) \overset{k}{\underset{\mu}{=\!=\!=}} \frac{2^{-l-2}}{\sqrt{\pi}}\, a^l \cdot p.\, G_{0,\,4}^{4,\,0}\left(\frac{a^2 p^2}{16}\,\bigg|\,\frac{1}{4}\pm\frac{\mu}{2},\frac{-l\pm\lambda}{2}\right)$$

and $p^{-l-\frac{1}{2}} f\left(\frac{1}{p}\right) \overset{k}{\underset{\mu}{=\!=\!=}} g(x)$

We obtain

$$\int\limits_0^\infty x^{-5/2}\, k_\lambda\left(\frac{a}{x}\right) f\left(\frac{1}{x}\right) dx =$$

$$\frac{2^{-l-2}}{\sqrt{\pi}} \int\limits_0^\infty a^l\, G_{0,\,4}^{4,\,0}\left(\frac{a^2 x^2}{16}\,\bigg|\,\frac{1}{4}\pm\frac{\mu}{2},\frac{-l\pm\lambda}{2}\right) g(x)\, dx$$

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Changing a in p and x into $\dfrac{i}{z}$ and multiplying by $\sqrt{\dfrac{2}{\pi}}\; p^{3/2}$ the left hand side can be shown to be $\psi(p)$ since

$$\psi(p) \xrightarrow{\;k\;} f(x),$$

giving

$$\psi(p) = \frac{2^{-l-3/2}}{\pi}\, p^{l+3/2} \int\limits_0^\infty G_{0,4}^{4,0}\left(\frac{p^2 x^2}{16}\;\middle|\;\frac{1}{4}+\frac{\mu}{2},\; \frac{1}{4}-\frac{\mu}{2},\; \frac{-l+\lambda}{2},\; \frac{-l-\lambda}{2}\right) g(x)\,dx$$

$$R(p) > 0$$

Hence the theorem.

Example 1:

Taking

$$g(x) = x^{l+1} J_\lambda(x)$$

We obtain (4, p. 137)

$$p^{-l-\frac{1}{2}} f\left(\frac{1}{p}\right) = \sqrt{\frac{2}{\pi}} \cdot \frac{2^{l+\frac{1}{2}}}{\Gamma(\lambda+1)}\, p^{-l-\frac{1}{2}-\lambda-\frac{1}{2}}\; \overline{|*}\left(\frac{\lambda\pm\mu+l+\frac{1}{2}}{2}+1\right)$$

$$\times {}_2F_1\left[\frac{\lambda\pm\mu+l+\frac{1}{2}}{2}+1;\; \lambda+1;\; -\frac{1}{p^2}\right] \qquad ;\; \begin{array}{l} R(\lambda) > -1 \\ R(\lambda+l) > |R(\mu)| - \dfrac{5}{2}. \end{array}$$

so that

$$f(x) = x^{\lambda+\frac{1}{2}} \sqrt{\frac{2}{\pi}} \cdot \frac{2^{l+\frac{1}{2}}}{\Gamma(\lambda+1)}\, \overline{|*}\left(\frac{\lambda\pm\mu+l+\frac{1}{2}}{2}+1\right) {}_2F_1\left[\begin{array}{c} \dfrac{\lambda\pm\mu+l+\frac{1}{2}}{2}+1;\; -x^2 \\ \lambda+1 \end{array}\right]$$

giving (4, p. 152)

$$\psi(p) = \frac{2^{\lambda+l+5/2}}{\pi}\, p^{l+2}\, \overline{|*}\left(\frac{\lambda\pm\mu+l+\frac{1}{2}}{2}+1\right) S_{-l-\lambda-3/2,\,\mu}^{(p)}$$

Where $S_{\nu,\,\mu}(z)$ is the Lommel Function.

Hence

$$\int\limits_0^\infty x^{l+1} G_{0,4}^{4,0}\left(-\frac{p^2 x^2}{16}\;\middle|\;\frac{1}{4}+\frac{\mu}{2},\; \frac{1}{4}-\frac{\mu}{2},\; \frac{-l+\lambda}{2},\; \frac{-l-\lambda}{2}\right) J_\lambda(x)\,dx$$

$$= 2^{\lambda+2l+4}\, \overline{|*}\left(\frac{\lambda\pm\mu+l+\frac{1}{2}}{2}+1\right) p^{\frac{1}{3}} S_{-l-\lambda-3/2,\,\mu}^{(p)}$$

$$R(p) > 0,\; R(\lambda) > -1,\; R(\lambda+l) > |R(\mu)| - 5/2,$$

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Example 2.

If we take

$$g(x) = x^{\rho - 1} {}_2F_1\left[\begin{array}{c} \alpha, \beta \\ \gamma \end{array} : (1 - x^2)\right]$$

then, Sharma (7, p. 116)

$$\dot{g}(x) = \sqrt{\frac{1}{\pi}} \frac{\Gamma(\gamma)\ x^{-l-\frac{1}{2}}}{\Gamma(\alpha)\,\Gamma(\beta)\,\Gamma(\gamma-\alpha)\,\Gamma(\gamma-\beta)}\ G^{2,4}_{4,2}\left(4x^2 \left|\begin{array}{c} \frac{1}{2}+\frac{\rho}{2}-\alpha,\ \frac{1}{2}+\frac{\rho}{2}-\beta,\ \frac{1}{4}\pm\frac{\mu}{2} \\ \frac{\rho}{2}-\frac{1}{2},\ \frac{\rho}{2}+\gamma-\alpha-\beta-\frac{1}{2} \end{array}\right.\right)$$

Now using (2, p. 209)

$$x^\sigma\ G^{m,n}_{p,q}\left(x\ \left|\begin{array}{c}\alpha_r \\ \beta_s\end{array}\right.\right) = G^{m,n}_{p,q}\left(x\ \left|\begin{array}{c}\alpha_r+\sigma \\ \beta_s+\sigma\end{array}\right.\right)$$

and (4, p. 153)

$$G^{m,n}_{p,q}\left(\lambda x^2\ \left|\begin{array}{c}\alpha_1...\alpha_p \\ \beta_1...\beta_q\end{array}\right.\right)^k_\nu = \frac{\lambda^{-\frac{1}{2}}}{2\sqrt{\pi}}\ p\ G^{n+2,\,m}_{q,\,p+2}\left(\frac{p^2}{4\lambda}\ \left|\begin{array}{c}\frac{1}{2}-\beta_1,\ ...,\ \frac{1}{2}-\beta_q \\ h,\ k,\ \frac{1}{2}-\alpha_1,\ ...,\ \frac{1}{2}-\alpha_p\end{array}\right.\right)$$

$$p+q < 2(m+n) \qquad\qquad h = \frac{1}{4}+\frac{\nu}{2},\quad k = \frac{1}{4}-\frac{\nu}{2}$$

$$|\arg\lambda| < (m+n-\tfrac{1}{2}p-\tfrac{1}{2}q)\ \pi,\ R(\beta_j) > \tfrac{1}{2}|R(\nu)| - \frac{3}{4},\ j=1,\,...\,m.$$

we obtain

$$\psi(\rho) = \frac{\Gamma(\gamma)\ 2^{l-\frac{3}{2}}\ p}{\pi\ \Gamma(\alpha)\,\Gamma(\beta)\,\Gamma(\gamma-\alpha)\,\Gamma(\gamma-\beta)} \times$$

$$G^{6,2}_{2,6}\left(\frac{p^2}{16}\ \left|\begin{array}{c}\frac{5}{4}-\frac{\rho}{2}+\frac{l}{2},\ \frac{5}{4}-\frac{\rho}{2}-\gamma+\alpha+\beta+\frac{l}{2} \\ \frac{1}{4}\pm\frac{\lambda}{2},\ \frac{1}{4}-\frac{\rho}{2}+\frac{l}{2}+\alpha,\ \frac{1}{4}-\frac{\rho}{2}+\frac{l}{2}+\beta,\ \frac{1}{2}+\frac{l}{2}\pm\frac{\mu}{2}\end{array}\right.\right)$$

$$R(\rho-l\pm\lambda) > 0,\ R(\gamma-\alpha-\beta) > 0,\ R(\mu\pm\mu+\tfrac{1}{2}) > 0$$

so that finally,

$$\int\limits_0^\infty x^{\rho-1}\ G^{4,0}_{0,4}\left(\frac{p^2x^2}{16}\ \left|\begin{array}{c}\frac{1}{4}+\frac{\mu}{2},\ \frac{1}{4}-\frac{\mu}{2},\ \frac{-l+\lambda}{2},\ \frac{-l-\lambda}{2}\end{array}\right.\right) {}_2F_1\left(\begin{array}{c}\alpha,\beta \\ \gamma\end{array} : 1-x^2\right)dx$$

$$= \frac{\Gamma(\gamma)\ 2^{2l}\ p^{-l-\frac{1}{2}}}{\Gamma(\alpha)\,\Gamma(\beta)\,\Gamma(\gamma-\alpha)\,\Gamma(\gamma-\beta)} \times$$

$$G^{6,\,2}_{2,\,6}\left(\frac{p^2}{16}\left|\begin{array}{l}\frac{5}{4}-\frac{\rho}{2}+\frac{l}{2},\ \frac{5}{4}-\frac{\rho}{2}-\gamma+\alpha+\beta+\frac{l}{2}\\[2mm]\frac{1}{4}\pm\frac{\lambda}{2},\ \frac{1}{4}-\frac{\rho}{2}+\frac{l}{2}+\alpha,\ \frac{1}{4}-\frac{\rho}{2}+\frac{l}{2}+\beta,\frac{1}{2}+\frac{l}{2}\pm\frac{\mu}{2}\end{array}\right.\right)$$

$$R\,(p)>0,\ R\,(r-l\pm\lambda)>0,\ R\,(\rho\pm\mu+\tfrac{1}{2})>0,\ R\,(\gamma-\alpha-\beta)>0$$

3. Theorem 2.

$$\text{If }\ \psi\,(p)\overset{k}{\underset{\mu}{=}}\ \phi\,(x)$$

$$p^{-\sigma+3}\,\phi\,(p)\overset{k}{\underset{\nu}{=}}\ f\,(x)$$

and

$$f\,(p)\overset{k}{\underset{\lambda}{=}}\ g\,(x)$$

then

$$\psi\,(p)=\frac{2^{\sigma-2}\,p^{3-\sigma}}{\pi^{3/2}}\int_0^\infty x^{-1}\,G^{2,\,4}_{4,\,2}\left(\frac{4}{x^2}\left|\begin{array}{l}\frac{7}{4}-\frac{\sigma}{2}\pm\frac{\mu}{2},\ \frac{1}{4}\pm\frac{\lambda}{2}\\[2mm]\frac{3}{4}\pm\frac{\nu}{2}\end{array}\right.\right)g\left(\frac{x}{p}\right)dx$$

provided the integral involved is convergent and

$$R\,(p)>0,\ R\,(\nu)<0,\ R\,(\nu\pm\lambda+\hat{\jmath})>0,\ R\,(\sigma)>|R\,(\mu)|+|R\,(\nu)|$$

Proof: Applying (2.1) to the functions (4, p. 145)

$$x^{\sigma-3/2}\,k_\mu\,(ax)\overset{k}{\underset{\nu}{=}}\frac{2}{\pi}\sqrt{\frac{p^{\nu+\frac{3}{2}}\,2^{\sigma-3}}{\Gamma\,(\sigma)}}\,a^{-\nu-\sigma}\,\overline{\Gamma_*}\left(\frac{\sigma\pm\mu+\nu}{2}\right)\overline{\Gamma_*}\left(\frac{\sigma\pm\mu-\nu}{2}\right)$$

$$\times\,{}_2\mathrm{F}_1\left(\frac{\sigma\pm\mu+\nu}{2}\,;\,\sigma:1-\frac{p^2}{a^2}\right)$$

and $\qquad\qquad R\,(\sigma)>|R\,(\mu)|+|R\,(\nu)|$

$$p^{-\sigma+3}\,\phi(p)\overset{k}{\underset{\nu}{=}}f\,(x)$$

therefore, since

$$\psi\,(p)\overset{k}{\underset{\mu}{=}}\phi\,(x)$$

$$(3.1)\ \psi(p) = \frac{2^{\sigma-2}\,p^{3-\sigma}}{\pi\,\Gamma(\sigma)}\, \overline{|_*}\left(\frac{\sigma\pm\mu+\nu}{2}\right)\overline{|_*}\left(\frac{\sigma\pm\mu-\nu}{2}\right)$$

$$\times \int_0^\infty x^{\nu+\frac{3}{2}}\,{}_2F_1\left[\frac{\sigma\pm\mu+\nu}{2}\ ;\ \sigma:\ 1-x^2\right] f(px)\,dx$$

Now Sharma (7, p. 116) has shown

$$x^{\rho-1}\,{}_2F_1\left[\begin{matrix}\alpha,\beta\\\gamma\end{matrix}\ ;\ 1-x^2\right] = \frac{k}{\lambda}\ \frac{\Gamma(\gamma)}{\sqrt{\pi}\ \Gamma(\alpha)\ \Gamma(\beta)\ \Gamma(\gamma-\alpha)\ \Gamma(\gamma-\beta)}\ G_{4,2}^{2,4}\left(\frac{4}{p^2}\ \Bigg|\ \begin{matrix}\frac{1}{2}\pm\frac{\rho}{2}-\alpha,\ \frac{1}{2}+\frac{\rho}{2}-\beta,\ \frac{1}{4}\pm\frac{\lambda}{2}\\ \frac{\rho}{2}-\frac{1}{2},\ \frac{\rho}{2}+\gamma-\alpha-\beta-\frac{1}{2}\end{matrix}\right)$$

also $\quad f(ap) = \dfrac{k}{\lambda}\ g\left(\dfrac{x}{a}\right)$

taking $\quad \rho=\nu+\dfrac{5}{2}, \quad \alpha=\dfrac{\sigma+\mu+\nu}{2}, \quad \beta=\dfrac{\sigma-\mu+\nu}{2}, \quad \gamma=\sigma$

and changing a into p,

we get after a little simplification

$$(3.2)\ \int_0^\infty x^{\nu+\frac{3}{2}}\,{}_2F_1\left(\frac{\sigma\pm\mu+\nu}{2}\ ;\ \sigma:\ 1-x^2\right) f(px)\,dx$$

$$= \sqrt{\frac{\Gamma(\sigma)}{\pi\ \overline{|_*}\left(\frac{\sigma\pm\mu+\nu}{2}\right)\overline{|_*}\left(\frac{\sigma\pm\mu-\nu}{2}\right)}}\ \times$$

$$\int_0^\infty x^{-1}\ G_{4,2}^{2,4}\left(\frac{4}{x^2}\ \Bigg|\ \begin{matrix}\frac{7}{4}-\frac{\sigma}{2}\pm\frac{\mu}{2},\ \frac{1}{4}\pm\frac{\lambda}{2}\\ \frac{3}{4}\pm\frac{\nu}{2}\end{matrix}\right)\ g\left(\frac{x}{p}\right)\,dx$$

so that with (3.1) and (3.2) we get the theorem under conditions stated.

Example Taking (4, p. 153)

$$g(x) = G_{h,k}^{m,n}\left(\alpha^2 x^2\ \Bigg|\ \begin{matrix}\alpha_1\dots\alpha_h\\ \beta_1\dots\beta_k\end{matrix}\right)$$

we have $f(x) = \dfrac{\alpha^{-1}}{2\sqrt{\pi}}\,x\,G_{k,h+2}^{n+2,m}\left(\dfrac{x^2}{4\alpha^2}\ \Bigg|\ \begin{matrix}\frac{1}{2}-\beta_1,\ \dots,\ \frac{1}{2}-\beta_k\\ \frac{1}{4}\pm\frac{\lambda}{2},\ \frac{1}{2}-\alpha_1,\dots,\frac{1}{2}-\alpha_h\end{matrix}\right)$

$$= \frac{1}{\sqrt{\pi}}\,G_{k,h+2}^{n+2,m}\left(\frac{x^2}{4\alpha^2}\ \Bigg|\ \begin{matrix}1-\beta_1,\ \dots\ 1-\beta_k\\ \frac{3}{4}\pm\frac{\lambda}{2},\ 1-\alpha_1,\ \dots\ 1-\alpha_h\end{matrix}\right)$$

so that $p^{-\sigma+3} \phi(p)$

$$= \frac{\alpha}{\pi} \, p \, G^{m+2,\,n+2}_{n+2,\,k+2} \left(a^2 p^2 \, \middle| \, \begin{matrix} -\frac{1}{4} \pm \frac{\lambda}{2}, \; -\frac{1}{2} + \alpha_1, \; \cdots \; -\frac{1}{2} + \alpha_h \\ \frac{1}{4} \pm \frac{\nu}{2}, \; -\frac{1}{2} + \beta_1, \; \cdots \; -\frac{1}{2} + \beta_k \end{matrix} \right)$$

Hence $\phi(x) = \dfrac{\alpha}{\pi} \, x^{\sigma-2} \, G^{m+2,\,n+2}_{h+2,\,k+2} \left(a^2 x^2 \, \middle| \, \begin{matrix} -\frac{1}{4} \pm \frac{\lambda}{2}, \; -\frac{1}{2} + \alpha_1, \cdots -\frac{1}{2} + a_h \\ \frac{1}{4} \pm \frac{\nu}{2}, \; -\frac{1}{2} + \beta_1, \; \cdots -\frac{1}{2} + \beta_k \end{matrix} \right)$

$$= \frac{\alpha^{-\sigma+3}}{\pi} \, G^{m+2,\,n+2}_{h+2,\,k+2} \left(\alpha^2 x^2 \, \middle| \, \begin{matrix} \frac{\sigma}{2} - \frac{5}{4} \pm \frac{\lambda}{2}, \; \frac{\sigma}{2} - \frac{3}{2} + \alpha_1, \; \cdots, \frac{\sigma}{2} - \frac{3}{2} + \alpha_h \\ \frac{\sigma}{2} - \frac{3}{4} \pm \frac{\nu}{2}, \; \frac{\sigma}{2} - \frac{3}{2} + \beta_1, \; \cdots, \frac{\sigma}{2} - \frac{3}{2} + \beta_k \end{matrix} \right)$$

whtch gives

$$\psi(p) = \frac{\alpha^{-\sigma+2}}{2 \, \pi^{3/2}} \, p \, \times$$

$$G^{n+4,\,m+2}_{k+2,\,h+4} \left(\frac{p^2}{4\alpha^2} \, \middle| \, \begin{matrix} \frac{5}{4} - \frac{\sigma}{2} \pm \frac{\nu}{2}, \, 2 - \frac{\sigma}{2} - \beta_1, \cdots 2 - \frac{\sigma}{2} - \beta_k \\ \frac{1}{4} \pm \frac{\mu}{2}, \; \frac{7}{4} - \frac{\sigma}{2} \pm \frac{\lambda}{2}, \; 2 - \frac{\sigma}{2} - \alpha_1, \cdots 2 - \frac{\sigma}{2} - \alpha_h \end{matrix} \right)$$

Therefore

$$\int_0^\infty x^{-1} \, G^{2,4}_{4,2} \left(\frac{4}{x^2} \, \middle| \, \begin{matrix} \frac{7}{4} - \frac{\sigma}{2} \pm \frac{\mu}{2}, \; \frac{1}{4} \pm \frac{\lambda}{2} \\ \frac{3}{4} \pm \frac{\nu}{2} \end{matrix} \right) G^{m,n}_{h,k} \left(\frac{\alpha^2 x^2}{p^2} \, \middle| \, \begin{matrix} \alpha_1 \cdots \alpha_h \\ \beta_1 \cdots \beta_k \end{matrix} \right) dx$$

$$= 2^{1-\sigma} \left(\frac{p}{2} \right)^{\sigma-2} G^{n+4,\,m+2}_{k+2,\,h+4} \left(\frac{p^2}{4\alpha^2} \, \middle| \, \begin{matrix} \frac{5}{4} - \frac{\sigma}{2} \pm \frac{\nu}{2}, \, 2 - \frac{\sigma}{2} - \beta_1, \, . \, 2 - \frac{\sigma}{2} - \beta_k \\ \frac{1}{4} \pm \frac{\mu}{2}, \; \frac{7}{4} - \frac{\sigma}{2} \pm \frac{\lambda}{2}, \, 2 - \frac{\sigma}{2} - \alpha_1, \cdots 2 - \frac{\sigma}{2} - \alpha_h \end{matrix} \right)$$

$$\left. \begin{array}{l} R(\beta_j) > \frac{1}{2} |R(\lambda)| - \frac{3}{4} \\ R(1 - \alpha_i) > \frac{1}{2} |R(\nu)| - \frac{3}{4} \\ R\left(\frac{\sigma}{2} + \beta_j\right) > \frac{1}{2} |R(\mu)| + \frac{3}{4} \end{array} \right\} \begin{array}{l} j = 1, \cdots m \\ i = 1, \cdots n \end{array} \quad h + k < 2(m+n)$$

$$\quad ; \quad |\arg(\alpha^2)| < (m + n - \tfrac{1}{2}p - \tfrac{1}{2}q)\pi$$

[206]

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THE SYSTEMS OF SODIUM MOLYBDATE WITH MINERAL ACIDS—PART I

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ABSTRACT

The systems of sodium molybdate with hydrochloric and nitric acids have been studied by conductivity and pH methods. The formation of polymolybdate ions are shown to be taking place through an intermediate molybdic acid which is formed by the hydrogen ions of the mineral acid. In sodium molybdate—hydrochloric acid system the aggregation appears to proceed up to the formation of a tetramolybdate and its hydrogen salt, while in sodium molybdate—nitric acid the aggregation proceeds to the formation of a hexamolybdate and its hydrogen salt. The greater degree of the aggregation in the latter system is attributed to the more soluble and more reactive hydrate $MoO_3.2H_2O$ produced by nitric acid on a normal molybdate. On ageing the poly-molybdates formed in both the systems hydrolyse to liberate free molybdic acid or their hydrogen salts, which are thrown out as precipitates at higher acid concentrations.

In earlier papers[1-4] we have reported the results of our studies on the system of sodium tungstate with mineral acids with special reference to (*i*) the effect of anion of the mineral acid used, on the formation of poly-tungstates, (*ii*) the effect of ageing on the systems, (*iii*) a probable mechanism of the formation of poly-tungstates and (*iv*) the effect of certain salts on the systems. Similar studies were carried out with systems of sodium molybdate with mineral acids and the results are reported in the present series. This paper describes the results of our study on the systems of sodium molybdate with hydrochloric and nitric acids.

EXPERIMENTAL

In the present work, $Na_2MoO_4. 2H_2O$ (A. R.), HCl (C. P.) and HNO_3 (C. P.) are used. The study of the systems is based on conductivity and pH measurements. Different sets of solutions were prepared to give molybdate/acid ratios ranging from 1:0 to 1:5 at concentrations M/16, M/32 M/64, and M/128 of sodium molybdate. The conductivity and pH of the systems were measured when fresh and after intervals of 2, 4, 8 and 12 weeks in order to study the effect of ageing. The results are; however, broadly shown (Figs. 1—4) under fresh and aged systems. Conductivity measurements were made on 'Doran' conductivity bridge using a well platinised conductivity cell. The pH measurements were made with a Beckman standard pH-meter using a glass electrode.

DISCUSSION

There has been a great deal of disagreement among different workers about the existence of various poly-molybdate ions in solution and their composition and constitution. The results of the conductometric titration of Jander[5] show discontinuities corresponding to the addition of 4, 7, 9 and 12 H^+ ions for every six MoO_4^{--} ions present in solution. From the conductometric results in conjunction with diffusion measusements, he came to the conclusion that at pH $14-6.5$ normal-, $6.3-4.5$ di-, $4.5-2.9$ para-, $2.9-1.5$ tri- and meta-, and at pH 1.25 octamolybdates are formed. Britzinger[5] supported the results of Jander from the measurements of electrodialysis of ions in acidified molybdate solutions. He could not, however, get evidence for the trimolybdate ion. Similar results were obtained by Ray and Sarma[6] by magnetic susceptibility method. Prior to the work of Jander, Dumanski and coworkers[7] showed from the measurements of electrical conductivity
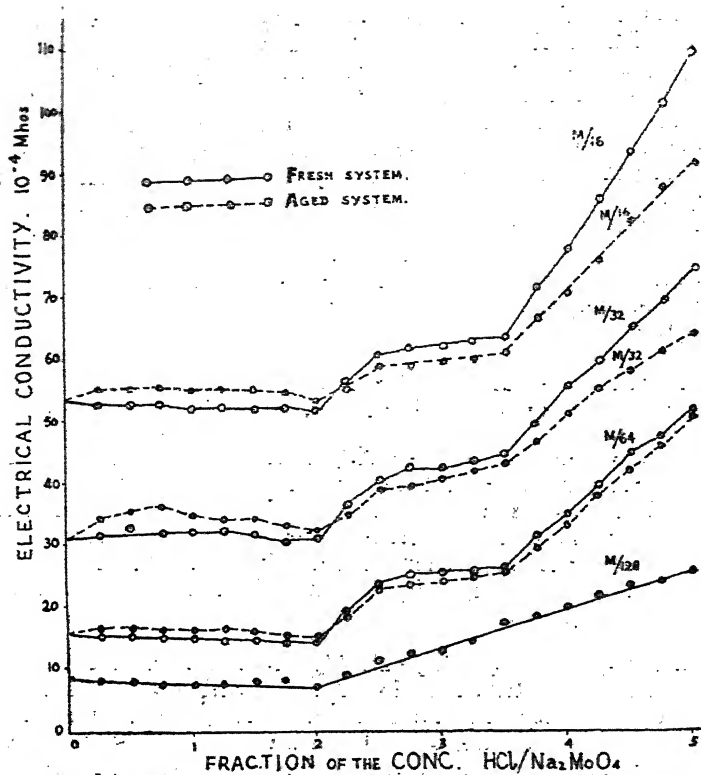
Fig. 1. Conductometric study of the system Sodium molybdate - Hydrochloric acid.
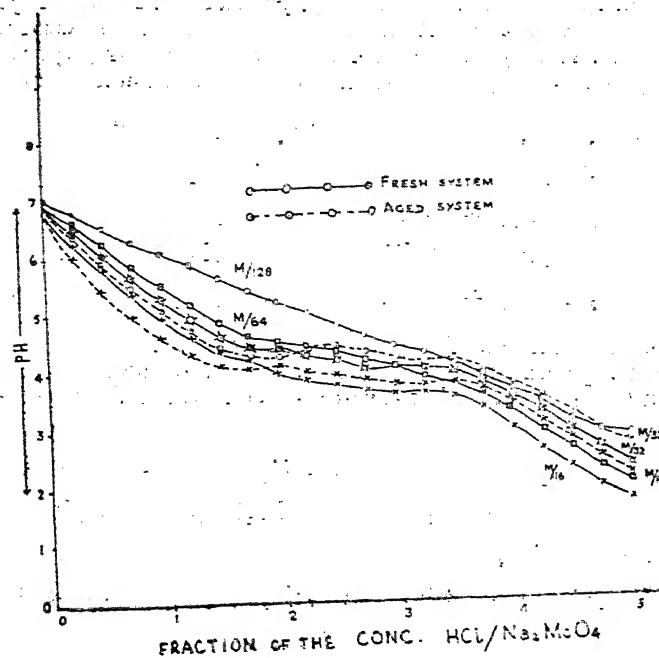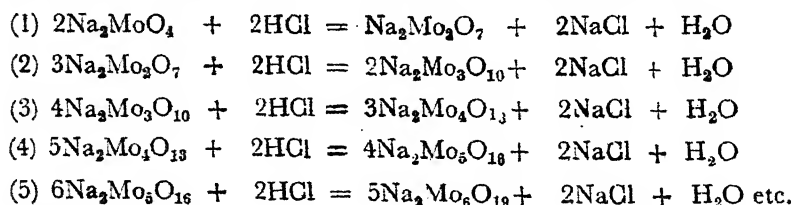

Fig. 2. pH study of the system of Sodium molybdate - Hydrochloric acid.

and depression of freezing point that on acidifying the normal sodium molybdate, the aggregation of the molybdate proceeded, depending on the concentration of the acid till a poly-molybdate of the composition $Na_2[O(MoO_3)_{4.5}]$ formed, which decomposed on further increase of acidity liberating highly ionised poly-molybdic acid in solution. Later the electrometric studies by Britton and German[8] gave support to the results of Dumanski and coworkers. Bevan[9] pointed out from conductivity and pH measurements that poly-molybdates and tungstates of the type $R_2[O(MoO_3)_4]$ are salts of very strong acids and do not completely decompose even in excess of acid solution. Ghosh and Biswas[10] calculated the equivalent conductivities of sodium poly-molybdates from the data obtained by Britton and German[11] and showed that what is believed by Britton and German to be a higher molybdate (possibly the octamolybdate) is really the hydrogen salt of the tetramolybdate $NaH[O(MoO_3)_4]$:

The conductivity results of the systems of sodium molybdate with hydrochloric and nitric acids as obtained in the present work are as follows :

(i) In the system Na_2MoO_4—HCl, as the concentration of HCl increases there is a gradual fall in the conductivity till the ratio, molybdate to HCl, reaches 1:2. Then there is a sudden rise in conductivity till the ratio is about 1:2·5, after which the results are steady up to the ratio 1:3·75. After·this there is an abrupt rise in the conductivity results showing thereby that there is no further action of HCl on the system (Fig. 1).

(ii) In the system Na_2MoO_4 – HNO_3, the fall of conductivity is similar but it continues till the ratio 1:3, after which there is a sudden rise in conductivity till the ratio 1:3·5 is reached. Thereafter the results are steady till 1:4, beyond which the conductivity rises sharply showing that there is no further action of the acid on the system, (Fig. 3).

Only recently the existence of $W_2O_7^{2-}$ and hence of $Mo_2O_7^{2-}$ have been proved[12] and in view of this fact the above observations of conductivity and pH results (Figs. 2 and 4) may be best explained by the following equations which show that the aggregation takes place gradually and in a continuous manner :

(1) $2Na_2MoO_4 \ + \ 2HCl = Na_2Mo_2O_7 \ + \ 2NaCl + H_2O$

(2) $3Na_2Mo_2O_7 \ + \ 2HCl = 2Na_2Mo_3O_{10} + \ 2NaCl \ + \ H_2O$

(3) $4Na_2Mo_3O_{10} \ + \ 2HCl = 3Na_2Mo_4O_{13} + \ 2NaCl \ + \ H_2O$

(4) $5Na_2Mo_4O_{13} \ + \ 2HCl = 4Na_2Mo_5O_{16} + \ 2NaCl \ + \ H_2O$

(5) $6Na_2Mo_5O_{16} \ + \ 2HCl = 5Na_2Mo_6O_{19} + \ 2NaCl \ + \ H_2O$ etc.

Again the direct formation of the poly-molybdates in the above equations can be represented through an intermmediate formation of molybdic acid before the polymerisation takes place. Thus the formation of a dimolybdate can be represented by

(6) $Na_2MoO_4 \ + \ 2HCl \quad = \ H_2MoO_4 \ + \ 2NaCl.$

(7) $Na_2MoO_4 \ + \ H_2MoO_4 = \ Na_2Mo_2O_7 + \ H_2O,$
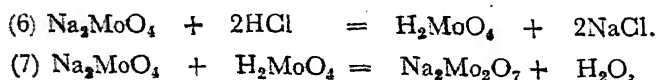
instead of by the equation,

(8) $2Na_2MoO_4 \ + \ 2HCl = Na_2Mo_2O_7 \ + \ 2NaCl \ + \ H_2O.$
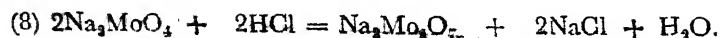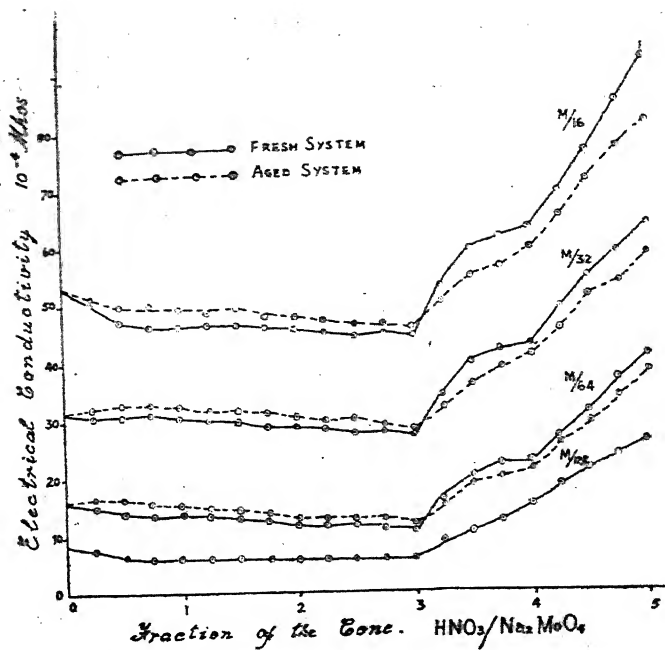
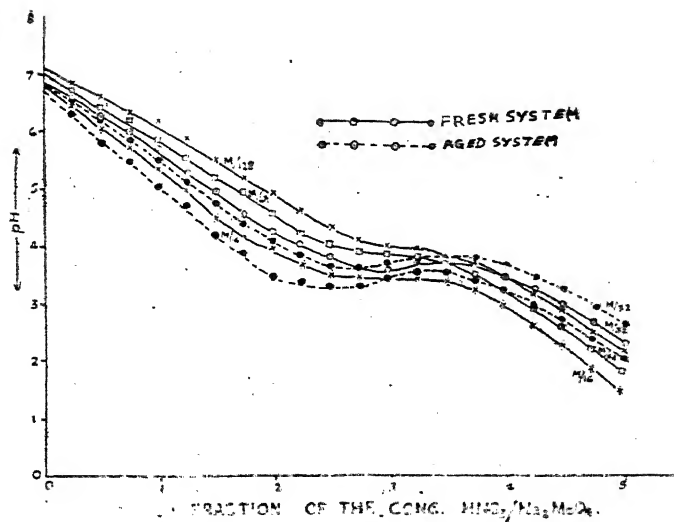Fig. 3.   Conductometric study of the system Sodium molybdate - Nitric acid.

Fig. 4.   pH study of the system Sodium molybdate - Nitric acid.

The polymerisation of molybdate through the intermediate formation of molybdic acid provides best explanation for the varying conductivity and pH results of the systems of sodium molybdate with different mineral acids. The anion of the mineral acid has a definite influence on the weak and amphoteric molybdic acid before it can bring about the aggregation. Ehrlich and Moser[13] have pointed out that tungstic acid is positively charged, and hence molybdic acid which is also a weak and amphoteric one. Because of the positive charge on the molybdic acid, the anions of the mineral acid are attracted by it and form a protective layer around the molybdic acid molecules and make them less reactive, thereby retarding the process of aggregation. The influence of the anion of a mineral acid in the process of aggregation is thus definite. The purpose of the hydrogen ion provided by the mineral acid is only to liberate the molybdic acid which in turn brings about the aggregation as shown in equations 6 and 7.

In the light of the above arguments the results obtained in the present work are explained as follows :

(i) *System* $Na_2MoO_4 - HCl$: The gradual and slight decrease in conductivity of the system up to the ratio 1:2 is due to the formation of successive poly-molybdates leading to the formation of the meta- or tetra-molybdates according to the equations 1, 2 and 3. The sharp rise in conductivity after the ratio 1:2 is due to the formation of the hydrogen salt of the tetramolybdate, the formation of which goes on till the ratio 1:3·75 is reached. The steady conductivity results between the ratios 1:2·5 to 1:3·75 indicate the completion of the formation of the hydrogen salt of the tetramolybdate. The sharp rise in conductivity again after the ratio 1:3·75 is due to the liberated tetramolybdic acid along with the non-reacting HCl.

(ii) *The system* $Na_2MoO_4 - HNO_3$: The fall in conductivity in this case till the ratio 1:3 is due to the formation of a hexamolybdate which requires 2·9 molecules of acid per molecule of sodium molybdate. The sharp rise in conductivity after this ratio is due to the formation of the acid hexamolybdate (similar to the acid tetramolybdate in the system $Na_2MoO_4 - HCl$). The steady conductivity between 1:3·5 to 1:4 is due to the completion of the formation of the acid molybdate. The sharp rise in conductivity again after the ratio 1:4 is due to the liberation of poly-molybdic acid along with non-reacting HNO_3. In fact the NO_3^- ion should have a greater effect on the molybdic acid than the chloride ion because of its larger ionic radius, and thus there should have been a retardation in the process of aggregation. But the litrature[14] on the subject describes the formation of $MoO_3.2H_2O$ by the action of nitric acid on a normal molybdate which is more soluble and reactive than the monohydrate $MoO_3.H_2O$ or H_2MoO_4. This acid is responsible for pushing the process of aggregation further than in the case with HCl, overcoming the effect of the anion NO_3^-.

The Factor of concentration of Na_2MoO_4 *on the system* : The results which have been so far discussed are for concentration M/16 of sodium molybdate of all the systems. The conductivity and pH of the systems were also studied at concentration of M/32, M/64, and M/128. All the inflections obtained at M/16 were also studied at concentrations M/32, and M/64 though not sharply. But in the case of concentration M/128, only one inflection at the point of completion of the aggregaton and then a sharp rise in conductivity occurred in all the systems. These results show that the process of aggreation of the molybdate in all the systems weakens with the decrease of concentration of sodium molybdate, though the same molybdate/acid ratios were maintained with all the concentration of sodium molybdate.

The effect of ageing on the systems : The conductivity and pH results of the aged systems of Na_2MoO_4 with mineral acids are shown along with the results of fresh systems. In the systems $Na_2MoO_4 - HCl$, there is a considerable increase in conductivity and a slight fall in the pH on ageing up to the ratio 1:2. This change is due to the hydrolysis of the polymolybdate formed in the fresh system. For example, the hyrolysis of a dimolybdate can be represented by the following alternate equations :

$$Na_2Mo_2O_7 \; + \; H_2O \; = \; 2NaHMoO_4$$

$$\text{or} \; Na_2Mo_2O_7 \; + \; H_2O \; = \; Na_2MoO_4 \; + \; H_2MoO_4$$
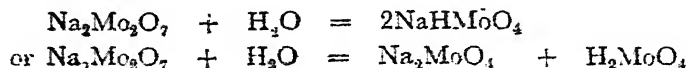
The hydrolysis giving the products according to the second equation is more probable than to the first one because the existence of a normal hydrogen molybdate is not known. After the point of completion of aggregation *i.e.* after the ratio 1:2, the system on ageing had thrown down certain insoluble products with a simultaneous fall in conductivity and increase in pH, which is due to the utilization of the free acid in forming insoluble precipitates. The results of the effect of ageing on the system of sodium molybdate with HNO_3 are similar to those with HCl. In these systems the effect of ageing is very significant at concentrations M/16 and M/32 while it was only slight at the concentration M/64 and M/128.

The composition, the constitution as well as the probable mechanism of the formation of the precipitates obtained on ageing from these systems and also from the systems with other mineral acids are discussed in a seperate paper.

In all the cases, the pH results are in accordance with those of the conductivity, and the same conclusions can be drawn from these also (Figs. 2 and 4). Hence no separate discussion is given with special reference to the pH measurements.

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THE REDUCTION OF PERMANGANATE AND MANGANESE
DIOXIDE BY TARTRATE

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ABSTRACT

The reductions of permanganate and manganese dioxide by tartrate ion have been studied iodometrically. It is attended with an induction period, which disappears if manganous ions are initially added. The induction period largely depends on the concentration of tartrate and very little on pH. The reaction towards the end depends mostly on pH. Results with manganese dioxide show that the yellow complex obtained towards the end of reduction of permanganate, is identical with the one obtained by dissolution of MnO_2. The slow decomposition of this complex is first order in oxidant, has a positive entropy change and anticatalysed by manganous ions.

Reduction of permanganate by tartaric acid has been studied by Hatcher and West[1,2], Dhar and coworkers[3,4], Garcia and coworkers[5-8], and Bhale and coworkers[9]. Dhar and coworkers reported that the reaction is attended with an induction period and the rate slightly decreases with the increase in concentration of the acid. Cabellow and Garcia[5] have found that the rate of reaction increases with the increase in concentration of acid and that Mn(II) acts as a catalyst in the beginning and as an anticatalyst towards the end. They also reported that hydrogen ions increase the induction period and hasten the breakdown of the yellow complex of Mn(III) and tartrate, reported by Perez and Garcia[7]. Lowering of the rate towards the end, in presence of manganous sulphate, has not been found by Bhale and coworkers[9].

It is well known that the reduction of permanganate takes place in several steps from Mn(VII) through Mn(VI), Mn(V), Mn(IV) and Mn(III) to Mn(II). Mn(VI) and Mn(V) states are stable only in high alkaline media. The two intermediate states stable in acid medium, are Mn(IV) or MnO_2 and Mn(III). Mn(III) as tripositive ion is stable only in high acid medium[10], but is quite stable ordinarily in the form of negative, complex ion[7]. We have studied the kinetics of the decomposition of the yellow tartrate complex of Mn(III), which is obtained by the dissolution of MnO_2 in tartaric acid. Manganese dioxide completely dissolves in about 10—15 minutes depending on pH of the system. Reduction of permanganate has also been studied to compare the results with those of other investigators. Mixtures of tartaric acid and potassium tartrate have been employed to note the effect of small variations in pH.

EXPERIMENTAL

All the chemicals used were either of B. D. H., A. R. or of E. Merck, G. R. quality. Stock solution of permanganate was prepared in boiled and cooled distilled water and standardised by sodium arsenite. Tartaric acid and potassium tartrate were also prepared in the usual way.

Fig. 1 — Changing the concentration of Tar.Acid

KMnO₄ : 0.01 N

pH

o 0.08 M Tar.Acid 2.35
△ 0.04 M Tar.Acid 2.65
× 0.02 M Tar.Acid 3.30
□ 0.01 M Tar.Acid 3.40

Fig. 2 — Effect of pH

KMnO₄ : 0.01 N

Tar.Acid K-Tar. pH

□ 0.08 M 2.35
o 0.06 M 0.02 M 3.15
× 0.05 M 0.03 M 3.60
△ 0.02 M 0.02 M 3.70

Fig. 3 — Effect of changing Tartarate and pH

KMnO₄ : 0.005N

Tar.Acid K-Tar. pH

× 0.02 M 0.01M 3.50
o 0.02 M 0 3.30
● 0.01 M 0.01M 3.70
△ 0.01 M 0 3.40

Fig. 4 — Effect of H₂SO₄ & MnSO₄

KMnO₄ : 0.005 N

Tar. Acid: 0.02 M
Pot.Salt : 0.01 M
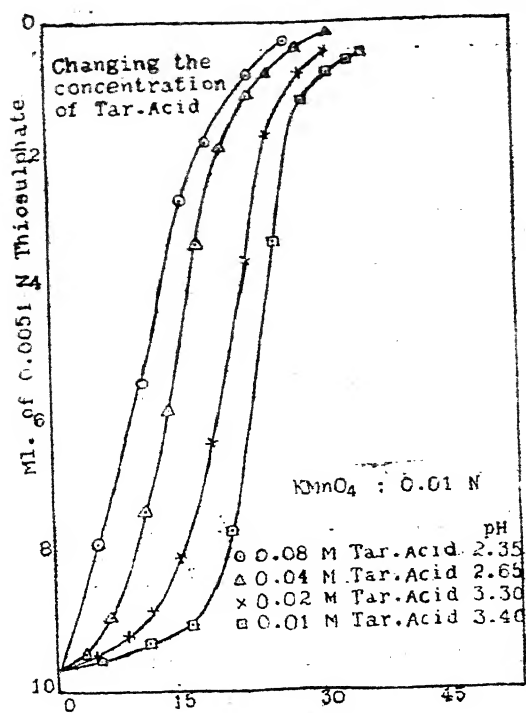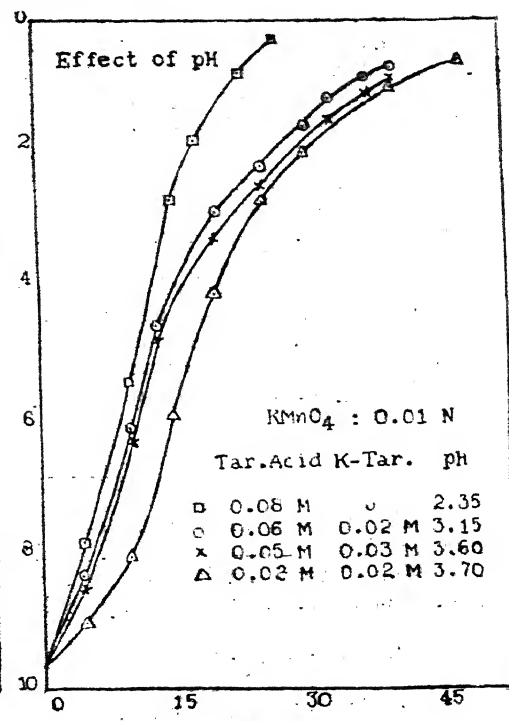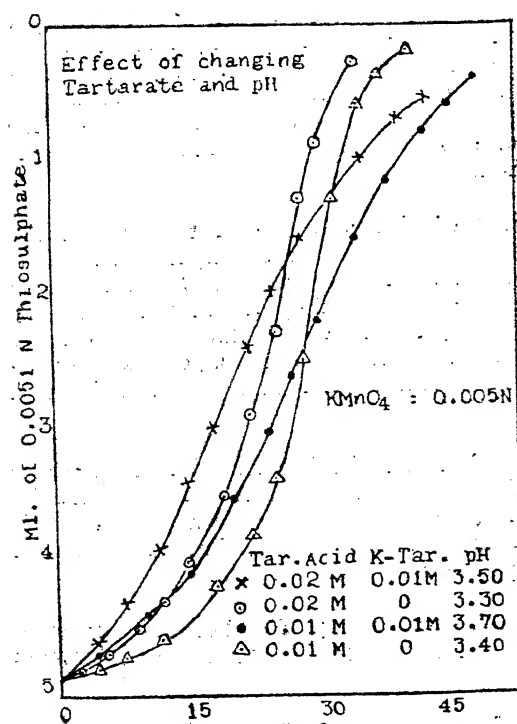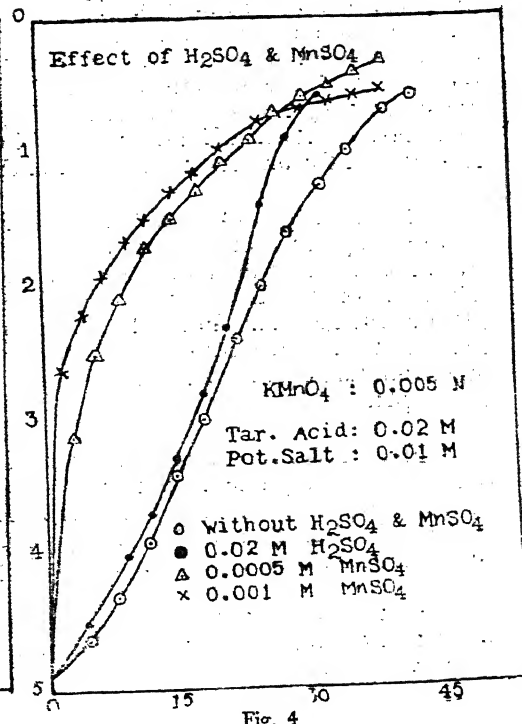
o Without H₂SO₄ & MnSO₄
● 0.02 M H₂SO₄
△ 0.0005 M MnSO₄
× 0.001 M MnSO₄

Time in minutes

The reaction was studied in a thermostat at 24°C. 5 ml. portions of the reaction mixture were taken out from the reaction vessel at suitable intervals of time and added to acidified 7% KI solution. The liberated iodine was estimated by 0·0051N sodium thiosulphate.

A suspension of manganese dioxide was prepared by mixing potassium permanganate and manganous sulphate in equivalent amounts together with a little of potassium sulphate and kept for about 24 hours. A black suspension was obtained which was washed free of sulphate ions, made up to a certain volume by means of water and standardised iodometrically against 0·0049N sodium thiosulphate. Care was taken to shake the vessel thoroughly before removing the suspension from the stock solution or from the reaction mixture. The reaction vessel was shaken by means of an electric shaker in order to check the particles of manganese dioxide from settling to the bottom, especially in the beginning of each run.

RESULTS AND DISCUSSION

The results with different concentrations of the acid and various mixtures are shown in figs. 1, 2 and 3 where d (oxidant)/dt curves are found to be 'S' shaped consisting of three portions as in case of oxalate[11] and malonate[12]. From these figures following conclusions may be drawn.

The reduction of permanganate has an induction period. The first autocatalytic process depends largely on the concentration of tartrate and very little on the hydrogen ion concentration. Fig. 2 gives the results where pH is varied and the concentration of tartrate is fixed. It may be seen that there is little effect, though pH changes from 2·35 to 3·60. However, with 0·02 M acid and 0·02 M salt (pH 3·70), the rate is slower than the mixture (0·05M : 0·03M) having 0·08 M overall concentration of tartrate. In this case there is a little change in pH, but the concentrations of the tartrate are in the ratio of 1:2. The same conclusion may be drawn from fig. 3 where 0·005 N KMnO₄ has been used. Fig. 1 clearly shows the combined effect of pH and tartrate ion concentration. The induction period is longest with the lowest concentration of the acid.

The third part of d (oxidant)/dt curves, which has been said to represent the slow decomposition of tartrate complex[7], largely depends on the hydrogen ion concentration and a little on the tartrate. From fig. 3 it is evident that whatever may be the nature of the curves in the beginning of the reaction, they lie in order of their pH towards the end. In fig. 2 towards the end, the curve for tartaric acid is far removed from other curves, and the curve for mixture, 0·02 : 0·02, comes closer to other mixture-curves because mixtures have similar pH and tartaric acid has a lower pH.

Fig. 4 gives the effect of manganous sulphate and sulphuric acid. In presence of manganous sulphate, induction period disappears and the rate increases with the increase in concentration of Mn(II). However, the rate is slowed down towards the end of reaction as has been reported by Cabellow and Garcia[5]. The effect of pH is further confirmed by the results in presence of sulphuric acid.

Results with manganese dioxide are shown in figs. 5 and 6. The reaction was found to be first order in oxidant i.e. Mn(III) and the constants were calculated from the relation.
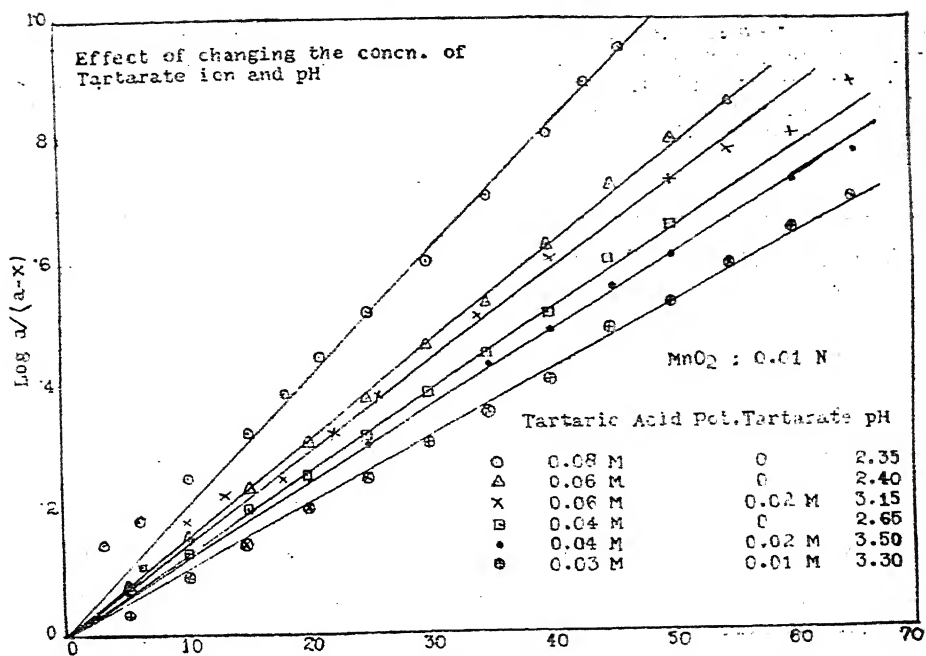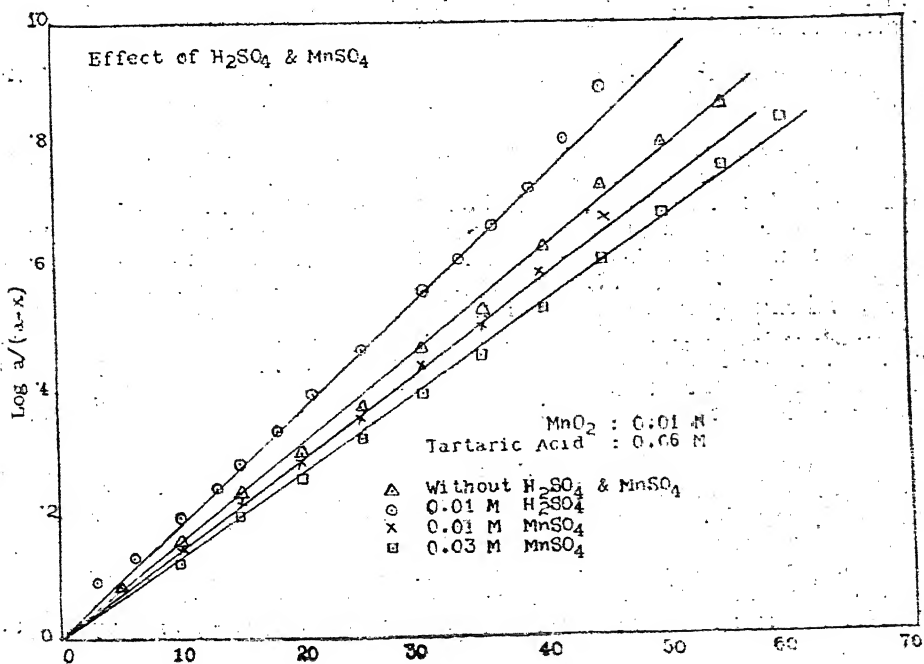
Fig. 5

Effect of changing the concn. of Tartarate ion and pH

Log a/(a-x)

MnO₂ : 0.01 N

	Tartaric Acid	Pot.Tartarate	pH
○	0.08 M	0	2.35
△	0.06 M	0	2.40
×	0.06 M	0.02 M	3.15
▣	0.04 M	0	2.65
●	0.04 M	0.02 M	3.50
⊖	0.03 M	0.01 M	3.30

Fig. 6

Effect of H₂SO₄ & MnSO₄

Log a/(a-x)

MnO₂ : 0.01 N
Tartaric Acid : 0.06 M

△	Without H₂SO₄ & MnSO₄
○	0.01 M	H₂SO₄
×	0.01 M	MnSO₄
▣	0.03 M	MnSO₄

Time in minutes

$$k = 2.303/t \times \log a/(a-x)$$

where a and $a-x$ are the concentrations of the oxidant initially and after time t. The results confirm the observations noted in the reduction of permanganate. Fig. 5 shows the results with the acid and the mixtures. In general, the reduction of yellow complex is much influenced by the hydrogen ion concentration. The constants are shown in table 1.

TABLE 1

Tartaric acid M	Pot. tartrate M	pH	$k \times 10^2$ min.$^{-1}$	
0.08	0	2.35	4.85	(a)
0.06	0.02	3.15	3.50	(b)
0.06	0	2.40	3.65	(c)
0.04	0.02	3.50	2.85	(d)
0.04	0	2.65	3.00	(e)
0.03	0.01	3.30	2.45	(f)

It is difficult to say how far the rate of decomposition of the complex depends on the concentration of tartrate. There is no doubt that it does depend to some extent as is seen by comparing the cases (b) and (f) or (d) and (f) in the above table. The order calculated by van't Hoff's differential method, ignoring the effect of pH, is found to be 0.5 with respect to tartrate ion.

Fig. 6 gives the catalytic effect of hydrogen ions and the anticatalytic action of Mn(II) as we have already seen in the reduction of permanganate.

The reaction with MnO$_2$ was studied also at higher temperatures, using 0.06 M concentration of tartaric acid and 0.01 N of MnO$_2$. The average constants were found to be 7.02×10^{-2} min.$^{-1}$ and 11.56×10^{-2} min.$^{-1}$ at 29° and 34°C respectively. The energy of activation and frequency factor for this range of temperatures were calculated to be 20790 cals and 1.41×10^{13} sec.$^{-1}$ respectively. The entropy of activation was + 0.68 E. U. It may be mentioned that Garcia[6] determined the energy and entropy of activation of the second slow process in the reduction of permanganate by tartaric acid. The entropy was always positive and the energy of activation was 28200 cals. Thus our results with MnO$_2$ indirectly confirm that the yellow complex of tartrate obtained in the reduction of KMnO$_4$, is identical with the yellow complex obtained by the dissolution of MnO$_2$ in tartaric acid.

The earlier reduction of permanganate to lowervalent manganese, possibly Mn(VI), is sufficiently slow. Mn(VI) immediately disproportionates[13] into Mn(VII) and MnO$_2$, especially in acid medium. In acid solution manganese dioxide reacts with tartaric acid producing Mn(III) which is ultimately reduced to Mn(II). The induction period is due to these series of steps in the beginning to reach a certain concentration of Mn(II), which may then directly react with permanganate producing Mn(III) according to the scheme suggested by Polissar[14], and by Gupta and Ghosh[15].

$$MnO_4^- + Mn^{++} \rightleftharpoons MnO_4^- + Mn^{+++}$$
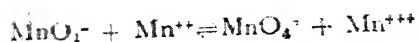
We have already reported that if manganous ions are initially added, no induction period is observed. The other slow process, the reduction of trivalent manganese complex, is first order in Mn(III) and has a positive entropy of activation. The reaction depends also on the concentration of tartaric acid. It appears that the slow process is between oppositely charged ions, most probably between tripositive manganese ion and negative tartrate ion. It is not possible to give the exact mechanism of this process because sufficient and requisite information about the effect of tartrate ion, could not be obtained.

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INFLUENCE OF CALCIUM-PHOSPHATES, ROCK PHOSPHATE AND BASIC SLAG ON LOSS OF NITROGEN FROM SODIUM NITRATE WHEN APPLIED TO SOIL ALONG WITH ORGANIC MATTER

By

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ABSTRACT

The loss of nitrogen from sodium nitrate when applied to soil can be markedly decreased if sodium nitrate is added to soils along with organic matter and different phosphates like monocalcium phosphate, di cal ium phosphate, tricalcium phosphate, basic slag and rock phosphate.

A long experience has shown that the artificial fertilizers are never as useful to the crops as they ought to be because when they are applied to the soils only a part of the nitrogen contained therein is utilized by the plants, while a good amount of nitrogen is lost (1, 2, 3). The exact manner in which the nitrogen is lost is not definitely known but leaching, denitrification and the formation and decomposition of the unstable substance ammonium nitrite have been suggested (4). In order to use the artificial fertilizers economically, there must be certain ways of retarding this type of nitrogen loss. The present study observes the influence of mono-calcium phosphate, di-calcium phosphate, tri-calcium phosphate, rock phosphate and basic slag when added to sodium nitrate in different doses to soil along with organic matter.

EXPERIMENTAL

The soil used for this experiment was collected from the fields infront of Sheila Dhar Institute of Soil Science, University of Allahabad, India. The soil under study was light grey to brownish black in colour and alluvial in origin and grows normal crops. Its chemical composition was determined by the methods recommended by Piper (5) and A. O. A. C. (6). Top nine inches of the soil was collected and passed through a 100 mesh sieve, after air drying. An amount of oven dried soil was taken to which when organic matter in the form of cow dung and/or phosphates were added, the total weight of the reacting mixture became 200 gms. The cow dung was added as 0·5% carbon. Five different phosphates *viz.* mono-calcium phosphate, di-calcium phosphate, tri-calcium phosphate, basic slag and rock phosphate were added as 0·5% P_2O_5. The reacting mixture was taken in 24 cm. enamel dishes. Nitrogen was added at the rate of 43 lbs, 86 lbs and 129 lbs per acre as sodium nitrate. The mixture was stirred on alternate days to make it homogenous and the moisture content was maintained at 20-25% by adding distilled water. This was kept in the laboratory at 27°C and samples were analyzed for total carbon (7) and nitrogen (8, 9).

The results obtained are recorded below.

TABLE 1

Percentage Composition of the soil used :—

Silica (HCl insoluble)	...	...	... 78·401
Loss on ignition	...	...	... 2·103
Sesquioxide	...	...	... 11·375
Fe_2O_3	...	...	... 4·520
CaO	...	...	... 3·318
MgO	...	...	... 1·640
K_2O	...	...	... 1·470
Total P_2O_5	...	...	... 0·219
Available P_2O_5	...	...	... 0·038

(1% citric acid soluble)

Al_2O_3	...	...	... 6·855
Exchangeable Calcium	...	...	... 6·66 m.e.%
Total carbon	...	...	... 0·1527
Total Nitrogen	...	...	... 0·0347
C/N ratio	...	...	... 4·4
Ammoniacal nitrogen	...	...	... 0·0026
Nitrate nitrogen	...	...	... 0·0017
Total available nitrogen	...	...	... 0·0043
Total/Available nitrogen	...	...	... 8·0

TABLE 2

Percentage composition of cow-dung used :—

Loss on ignition	...	...	...	... 63·460
Ash	...	...	...	... 36·530
Silica	...	...	...	... 30·660
Calcium-oxide	...	...	...	... 2·520
Magnesium-oxide	...	...	...	... 0·934
Potassium-oxide		...	...	... 0·721
P_2O_5		...	...	... 0·673
Total carbon		...	...	... 28·6300
Total nitrogen		...	...	... 1·0108
C/N ratio		...	...	... 28·34

TABLE 3
Percentage Analysis of Rock-phosphate and Basic slag

		Rock phosphate	Basic Slag
Silica	...	6·300	23·660
Calcium-oxide	...	20·800	34·360
Magnesium-oxide	...	1·920	5·280
Fe_2O_3	...	4·200	11·720
Al_2O_3	...	26·900	...
K20	...	...	9·070
Total P_2O_5	...	27·800	7·590
Available P_2O_5	...	1·000	4·460
(1% Citric acid soluble)			

TABLE 4
Effect of phosphate on loss of nitrogen from sodium nitrate when added at the rate of 43 lbs of nitrogen per acre to the soil

	% loss of Nitrogen at the end of 60 days	% loss of N_2 at the end of 120 days
Soil + cow dung + Sodium nitrate	16·8	34·3
Soil + cow dung + sodium nitrate + mono calcium phosphate.	14·0	25·6
Soil + cow dung + sodium nitrate + di calcium phosphate.	12·0	23·8
Soil + cow dung + sodium nitrate + tri calcium phosphate.	12·9	24·7
Soil + cow dung + sodium nitrate + basic slag.	13·2	25·0
Soil + cow dung + sodium nitrate + rock phosphate.	13·7	25·4

TABLE 5
Effect of phosphate on loss of nitrogen from sodium nitrate when added at the rate of 86 lbs of nitrogen per acre to the soil

	% loss of nitrogen at the end of 60 days	% loss of nitrogen at the end of 120 days
Soil + cow dung + sodium nitrate	19·0	37·1
Soil + cow dung + sodium nitrate + mono calcium phosphate.	16·4	28·3
Soil + cow dung + sodium nitrate + di calcium phosphate.	14·2	26·0
Soil + cow dung + sodium nitrate + tri calcium phosphate.	15·3	27·2
Soil + cow dung + sodium nitrate + basic slag.	15·5	27·6

TABLE 6

Effect of phosphate on loss of nitrogen from sodium nitrate when added at the rate of 129 of nitrogen per acre to the soil

	% loss of nitrogen at the end of 60 days	% loss of nitrogen at the end of 120 days
Soil + cow dung + sodium nitrate	21·6	39·3
Soil + cow dung + sodium nitrate + mono calcium phosphate.	18·6	33·1
Soil + cow dung + sodium nitrate + di calcium phosphate.	16·4	30·8
Soil + cow dung + sodium nitrate + tri calcium phosphate.	17·5	32·0
Soil + cow dung + sodium nitrate + basic slag.	17·8	32·3
Soil + cow dung + sodium nitrate + rock phosphate.	18·2	32·8

DISCUSSION

The above results show that a part of the nitrogen added as sodium nitrate is lost with lapse of time. The loss is more marked at the end of 120 days than at the end of 60 days. The loss of nitrogen increases with increasing doses of sodium nitrate.

When different phosphates are added along with organic matter in the form of cow dung, the loss of nitrogen is retarded. The efficiency of different phosphates in checking the loss of nitrogen from sodium nitrate is of the following order : —

$$CaHPO_4 > Ca_3(PO_4)_2 > \text{ basic slag } > \text{ rock phosphate } > Ca(H_2PO_4)_2$$
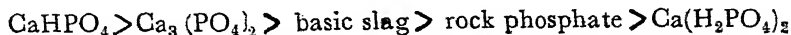
It appears that the addition of different phosphates along with organic matter fixes atmospheric nitrogen in the soil due to the oxidation of the organic matter. Since the total nitrogen determinations measures the balance of nitrogen loss and nitrogen gain, the net result appears to be the retardation of the loss of nitrogen from sodium nitrate (10, 11).

Phosphates also reduce the loss of nitrogen from sodium nitrate by forming stable phosho-proteins, nucleo-proteins and other complexes of this nature by the combination of proteins of the soil and the added phosphates (12). These more stable complexes seem to resist nitrification and ammonification better than protein alone and thus the loss of nitrogen is decreased in presence of phosphate than in its absence.

Moreover the calcium ions introduced along with these phosphate may react with the unstable substance ammonium nitrite and form more stable calcium nitrite. Ammonium nitrite may normally be formed from nitrate ion of sodium nitrate by de-nitrification and reaction with ammonium ions which are obtained as a result of oxidation of proteins and other nitrogenous substances present in the soil. Thus the possibility of formation of ammonium nitrite is less in presence of calcium ions.

Further, the decomposition of ammonium nitrite is increased by the presence of acids, which may be formed due to the oxidation of organic matter, but in presence of phosphates which act as buffer, an increase in the acidity is checked and hence the decomposition of ammonium nitrite is also retarded considerably.

Hence overall effect of addition of phosphates is the retardation of nitrogen loss from sodium nitrate when added to the soil, along with organic matter.

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THE SYSTEM OF SODIUM MOLYBDATE WITH MINERAL ACIDS—PART II

By

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ABSTRACT

The systems of sodium molybdate with sulphuric and phosphoric acids have been studied by conductivity and pH methods. The results obtained with sodium molybdate-sulphuric acid system are mostly similar to those with hydrochloric and nitric acids. However in this system the sulphate ion retards the formation of the polymolybdates in the initial stages which is overcome by the increase in H^+ ion concentration. The poly-molybdates formed in this system undergo hydrolysis on a ageing. Phosphoric acid is found to be, as such, ineffective in bringing about the aggregation of molybdate ions to form poly-molybdate ions.

In Part I of this paper[1] the results of our study of the systems of sodium molybdate with hydrochloric and nitric acids have been discussed. This part describes the study of the system of sodium molybdate with sulphuric and phosphoric acids. For this study, $Na_2 MoO_4. 2H_2O$ (A.R.), H_2SO_4 (C. P.) and H_3PO_4 (C. P.) are used. The study of these systems also is based on conductivity and pH measurements. Different sets of solutions were prepared to give molybdate/acid ratios ranging from 1:0 to 1:5 at concentrations $M/16$, $M/32$, $M/64$, $M/132$ of sodium molybdate. The conductivity and pH of the systems were measured when fresh and after intervals of 2, 4, 8 and 12 weeks in order to study the effect of ageing. The results, however, have been shown broadly under fresh and aged systems (Figs. 1 to 4).

DISCUSSION

The results of the system sodium molybdate-sulphuric acid are different from those with HCl and HNO_3. Here, the conductivity falls abruptly up to the ratio 1:0·5 and there is turbidity in the solution. The conductivity then gradually increases till the ratio 1:2, after which again there is a fall in conductivity till the ratio 1:4 is reached. Thereafter the conductivity rises sharply indicating that there is no further action of the acid on the system. In the system sodium molybdate-phosphoric acid, there is a slight fall in conductivity up to the ratio 1:2·5, after which there is a gradual and slight increase in conductivity. These observations are explained as follows in the light of the arguments given in Part I of this paper in connection with the formation of the poly-molybdate ions :

(i) *The system sodium molybdat sulphuric acid :* The slight turibidity and the fall of conductivity in this system before the ratio 1:0·5 is reached is due to the liberation of free and insoluble molybdic acid. The slight increase in the conductivity after this ratio till 1:2 is due to the liberation of free and insoluble molybdic acid. The slight increase in the conductivity after this ratio till 1:2 is due to the liberation of molybdic acid in solution without being reacted with Na_2MoO_4 to bring about the aggregation. Here the SO_4^{--} ion has effect on the
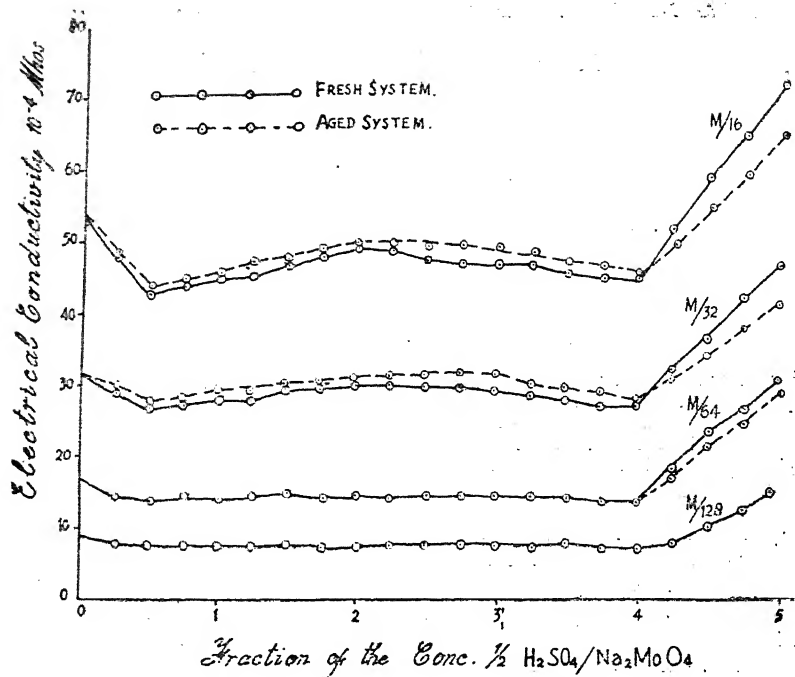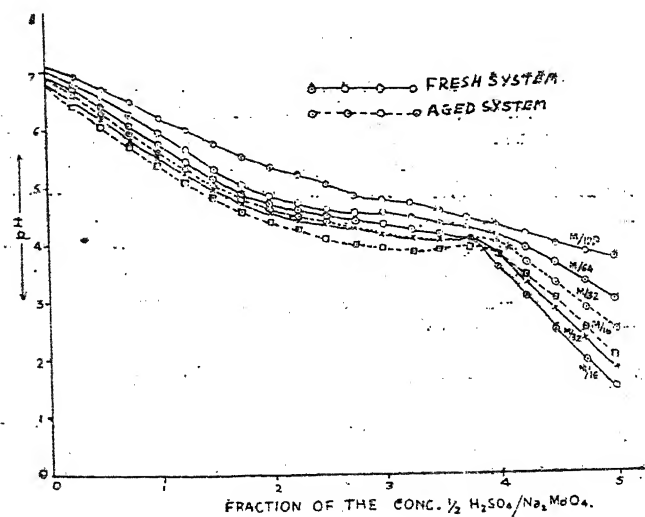
[225]

Fig. 1. Conductometric study of the system Sodium molybdate - Sulphuric acid.

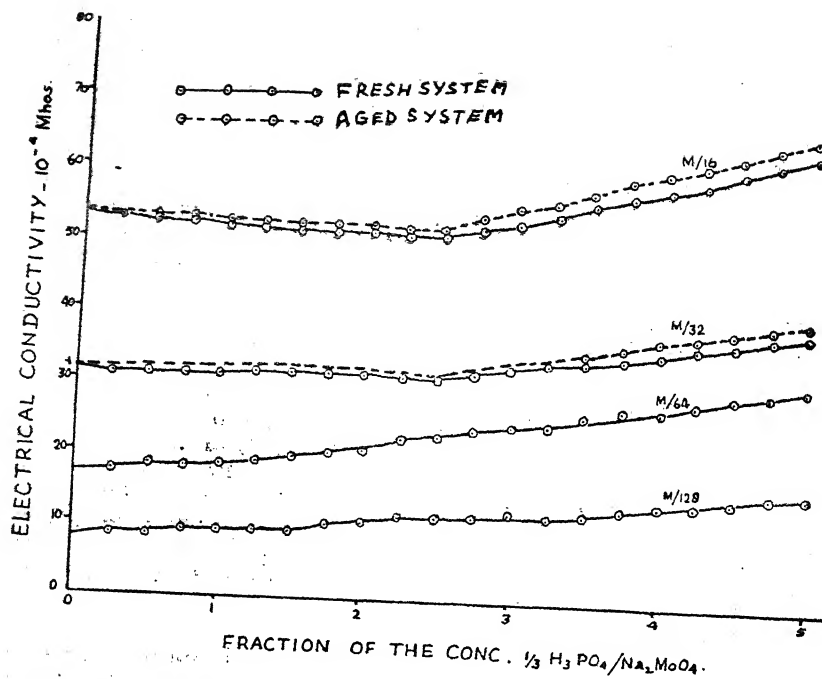Fig. 2. pH study of the system Sodium molybdate - Sulphuric acid.

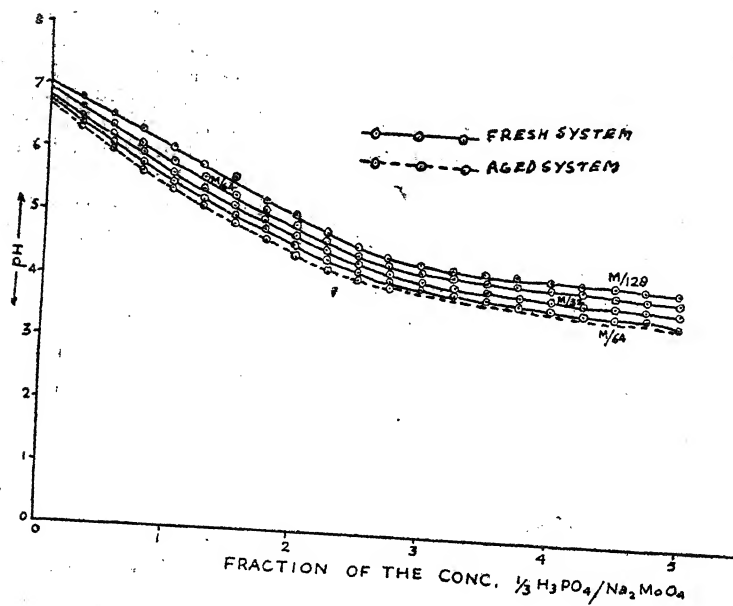Fig. 3. Conductometric study of the system Sodium molybdate - Phosphoric acid.

Fig. 4. pH study of the system Sodium molybdate - Phosphoric acid.

[227]

positively charged molybdic acid. It forms a protective layer by virtue of its large ionic radius and high negative charge. However, with the increase of H^+ ions (*i.e.* after the ratio 1:2) the anionic effect is overcome and aggregation takes place till the ratio 1:4 is reached, which is indicated by the fall of condcutivity in that region. After the ratio 1:4, there is the usual rise in conductivity showing that there is no further action of the acid on the system. The aggregation in this system also appears to be up to the formation of a tetramolybdate because the process of aggregation shown by the fall of conductivity is in between two units of the acid (*i.e.* between 1:2 to 1:4). However there is no further inflection in this system which shows that the acid tetramolybdate is not formed. After the rotio 1:4, the sharp rise in conductivity is due to the presence of free non-reacting sulphuric acid.

(ii) *The System sodium molybdate - phosphoric acid* : Phosphoric acid is a week mineral acid and the results evidently show that it is not strong enough to bring about the formation of poly-molybdates. The slight fall in conductivity upto 1:2·4 is due to the formation of lower poly-molybdates as in the case with acetic acid[2]. There is no sharp rise in conductivity to show the completion of the formation of poly-molybdates as in the case of other mineral acids. The pH results also show that the pH required for the formation of higher poly-molybdates is not reached in this system.

The factor of concentration of sodium molybdates :—The factor of concentration of sodium molybdate in these system was found to be the same as for the systems studied in Part I of this paper. That is, the results are quite pronounced at concentrations M/16 and M/32 and no sharp inflections are obtained at M/64 and M/128 of sodium molybdate.

The effect of ageing on the systems :—The effect of ageing on the system of sodium molybdate with sulphuric acid is similar to those with HCl and HNO_3. That is, on ageing, the poly-molybdates formed in the systems with sulphuric acid also had undergone hydrolysis with the liberation of molybdic acid or acid molybdates resulting in the fall in conductivity and rise of pH. At higher acid concentrations, on ageing, the precipitates are formed in this system also and the nature of these precipitated products is discussed in a future communication. However, there is practically no change, on ageing, in the system with phosphoric acid excepting a slight increase in conductivity at the initial acid concentrations.

In all the cases the pH results (Figs. 2 and 4) are in accordance with those of the conductivity, and the same conclusions can be drawn from these also.

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CONTENTS